Supplementary Information

SI-Tables 1, 2: Input and output lattice parameters GGA+U DFT calculations

Table SI-1. Lattice parameters of α-Li_3FeF_6: Structural input for spinrelaxed calculations, U=5eV, k-mesh = 2x2x3, PW91 and refined lattice parameters.

Magnetic moment Fe	a [Å]	b [Å]	c [Å]	V [$Å^3$]
α-Li_3FeF_6, exp. [18]	14,4277	8,6810	10,0441	1251,68
5 (d^5), HS#	14,6560	8,7574	10,1666	1305,79
1 (d^5), LS	14,5698	8,5815	10,2198	1277,12

Table SI-2. Lattice parameters of Li_2FeF_6 and Li_4FeF_6: Structural input for spinrelaxed calculations, U=5eV, k-mesh = 2x2x3, PW91 and refined lattice parameters.

Magnetic moment Fe	a [Å]	b [Å]	c [Å]	V [$Å^3$]
Li_2FeF_6	14,7287	8,4933	9,6080	1201,92
4 (d^4), HS#	14,9223	8,8165	10,0460	1313,21
2 (d^4), LS	14,9049	8,8113	9,9608	1310,37
Li_4FeF_6	14,3781	8,4669	9,8088	1194,11
4 (d^6), HS#	14,7798	8,7532	10,1721	1314,57
0 (d^6), LS	14,6891	8,5629	9,9603	1252,01

refined/optimized lattice parameters of structures used for voltage and DOS calculations (lowest total energy)

Our calculations do not predict a magnetic moment on either the fluorine or lithium atoms.

SI tables 3: Voltage data

Table SI-3. Voltage data derived from total Energies of the most stable HS relaxed P1 structures.

Structure	Total Energy [eV]	Voltage [V]
HS-Li_2FeF_6	-508,204572	6.11
HS-α-Li_3FeF_6	-604,573591	
HS- Li_4FeF_6	-663,039575	2.95

Refering to equation (1) in the manuscript: Metallic lithium was used to calculate the chemical potential of a single lithium atom using VASP:
μ(Li) = -1.9177eV