Electronic Supplementary Material (ESI) for Dalton Transactions.

Intimately mixed copper, cobalt, and iron fluorides resulting from the insertion of fluorine into a LDH template

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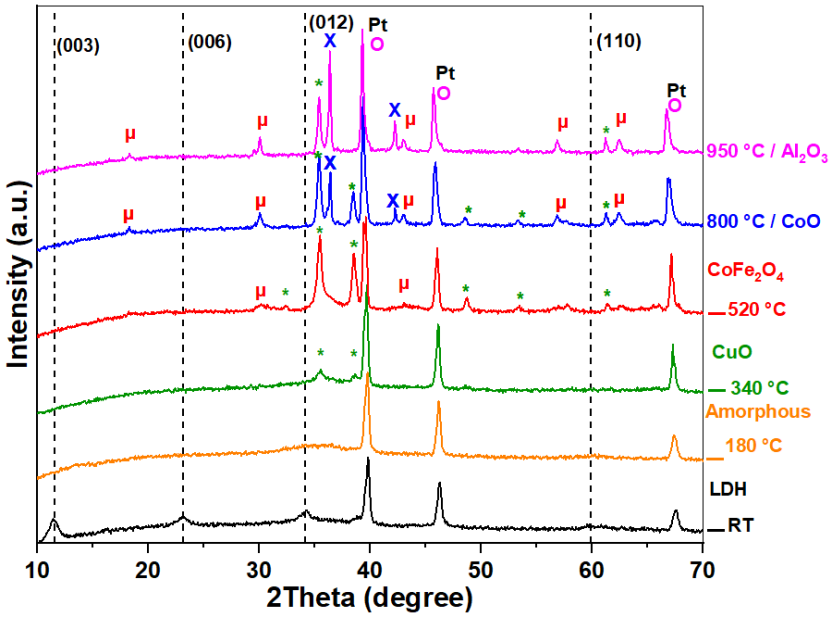

Fig. S1 Phase identification in diffractograms across critical temperatures.

* CuO (96-901-6823), **µ** $CoFe_2O_4$ (96-153-3163),

x CoO(96-900-8619), and **o** Al_2O_3 (96-154-1583)

Table S1 Detail of experimental composition calculations obtained by ICP-AES.

Stoichiometric coefficients	Equations	Results
x	$\frac{Cu\ (\%)}{Co\ (\%)} = \frac{(1-x)MCu}{x\ MCo} = 3.34$	0.24
y	$\frac{Fe\ (\%)}{Al\ (\%)} = \frac{y\ MFe}{(1-y)\ MAl} = 5.32$	0.72
n	$\frac{\frac{Cu\ (\%)}{M\ Cu} + \frac{Co\ (\%)}{M\ Co}}{\frac{Al\ (\%)}{M\ Al} + \frac{Fe\ (\%)}{M\ Fe}}$	2.03

z	2n(1+x) + 2nx + 3(1-y) + 3y -6 - z = 0	1.07

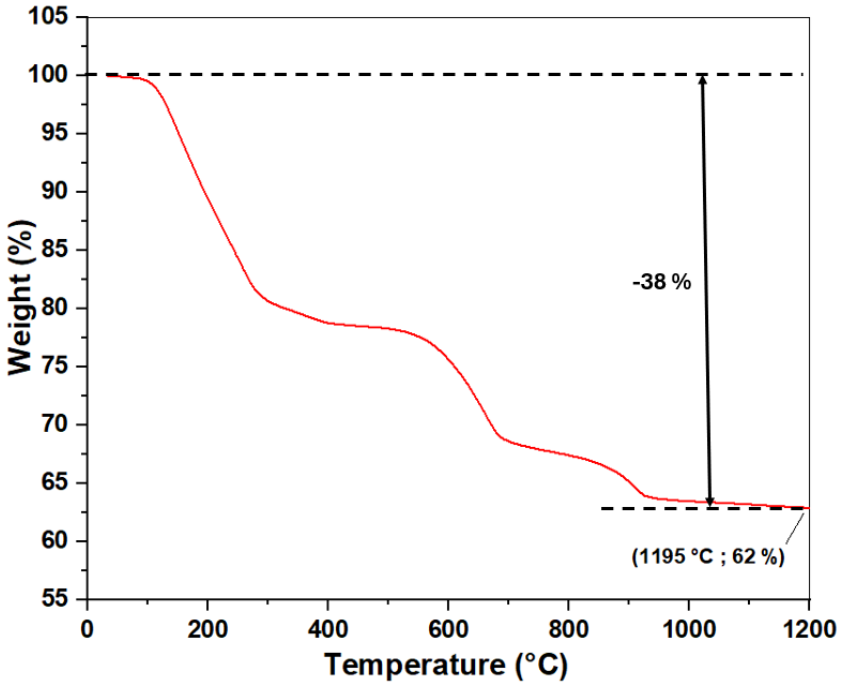

Fig. S2 Thermogravimetric analysis of LDH template under helium, temperature ramp from RT to 1200 °C at 10 °C/min.

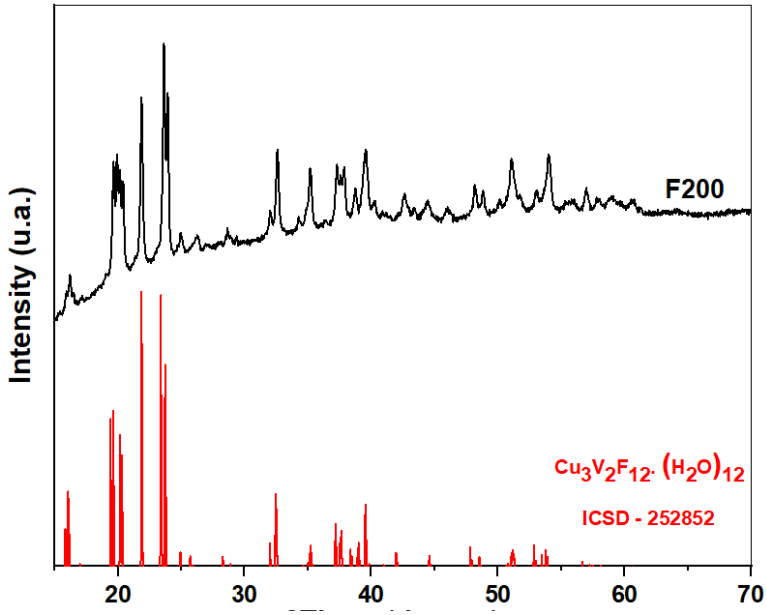

Fig. S3 Diffraction peak attributions of fluorinated LDH at 200°C (F200) after its exposure to air.

Table S2 Compositions generated by semi-quantitative EDX analysis (% Atomic).

Elements	Cu	Co	Al	Fe	Cl	F
LDH Template	8.2	1.03	2.19	3.9	1.13	0
F200	12.6	1.83	2.4	5.17	0.2	31

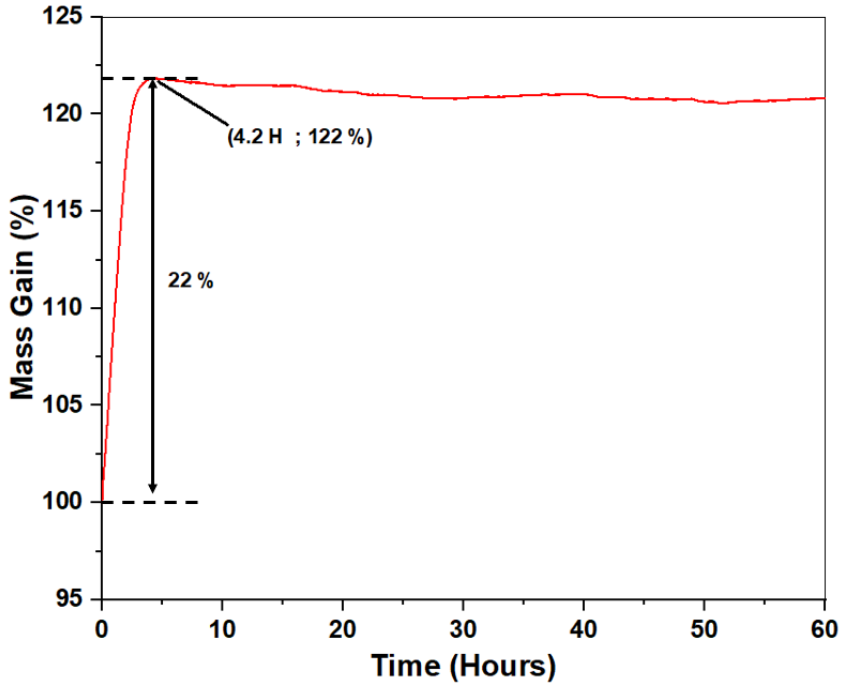

Fig. S4 Thermogravimetric study of water uptake at 30°C Over 60 hours in freshly synthesized F200.

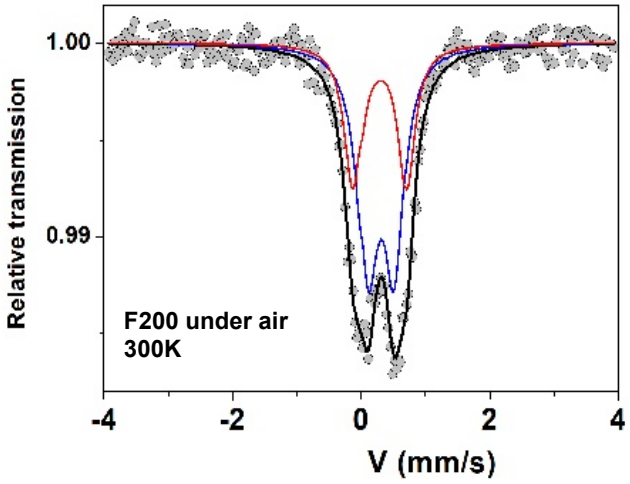

Fig. S5 Mössbauer spectra at 300 K for F200 under air phase. Grey dots represent the experimental data, black lines the resulting fitted spectra

Table. S3 Data collection, structural parameter and atomic positions of $Cu_3Fe_{1.5}Al_{0.5}F_{12}\cdot(H_2O)_{12}$

Cell parameters		Bond distances			
a (Å)	7.4836(4)	Atom i	Atom j		d_{i-j} (Å)
b (Å)	7.5759(5)	Cu1	F1	2x	1.89(3)
c (Å)	8.1753(5)		Ow2	2x	2.30(3)
α (°)	88.826(5)		Ow1	2x	2.38(3)
β (°)	89.927(6)	Cu2	Ow3	2x	2.04(3)
γ (°)	87.934(6)		F3	2x	2.13(3)
V (Å^3)	463.10(5)		F3	2x	2.13(3)
Z	1		Ow4	2x	2.19(3)
ρ (g/cm^3)	2.538	Cu3	Ow5	2x	2.01(3)
SG	*P*-1		Ow6	2x	2.18(3)
Symmetry	Triclinic		F2	2x	2.22(3)
R_p/R_{wp}	0.137/0.095	Fe1|Al2	F1	2x	2.05(3)
R_b/R_f	0.036/0.032		F2	2x	2.11(3)
χ^2	2.19		F3	2x	2.31(3)
		Fe2|Al1	F5	2x	1.80(3)
			F6	2x	1.94(3)
			F4	2x	1.99(2)

Atom	Wyck.	X	Y	Z	B(Å^2)*	Occ.
Cu1	1a	0	0	0	1.0	1
Cu2	1g	0	½	½	1.0	1
Cu3	1e	½	½	0	1.0	1
Fe1	1c	0	½	0	1.0	0.75
Fe2	1f	½	0	½	1.0	0.75
Al1	1f	½	0	½	1.0	0.25
Al2	1c	0	½	0	1.0	0.25
Ow1	2i	0.1040(39)	0.0812(42)	-0.2646(38)	1.0	1
Ow2	2i	0.2801(44)	0.0326(39)	0.1072(46)	1.0	1
Ow3	2i	0.2575(38)	0.4587(37)	0.4242(39)	1.0	1
Ow4	2i	0.0573(43)	0.7730(44)	0.5597(38)	1.0	1
Ow5	2i	0.4068(47)	0.6022(42)	-0.2140(40)	1.0	1
Ow6	2i	0.4787(44)	0.7573(41)	0.1148(37)	1.0	1
F1	2i	0.9311(36)	0.2414(36)	0.0181(37)	1.0	1
F2	2i	0.2444(37)	0.4234(35)	0.1127(31)	1.0	1
F3	2i	0.1019(35)	0.4444(40)	0.7386(40)	1.0	1
F4	2i	0.4583(42)	0.2510(34)	0.5623(30)	1.0	1
F5	2i	0.5847(43)	0.0640(36)	0.3029(25)	1.0	1
F6	2i	0.2618(40)	-0.0098(32)	0.4062(38)	1.0	1

**Atomic displacements were not refined and fixed at 1.0*

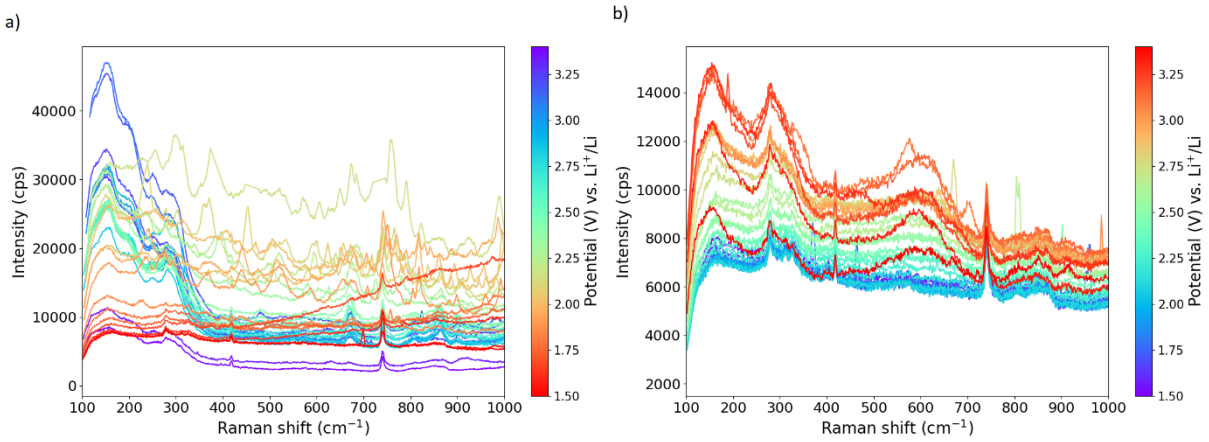

Fig. S6 Raman *operando* of the fluorinated active material with 1M LiTFSI in TEGDME electrolyte, one scan out of 5 between: (a) 3.4V and 1.5 V vs. Li^+/Li during electrochemical reduction; (b) 1.5 and 3.5 V vs. Li^+/Li during electrochemical oxidation

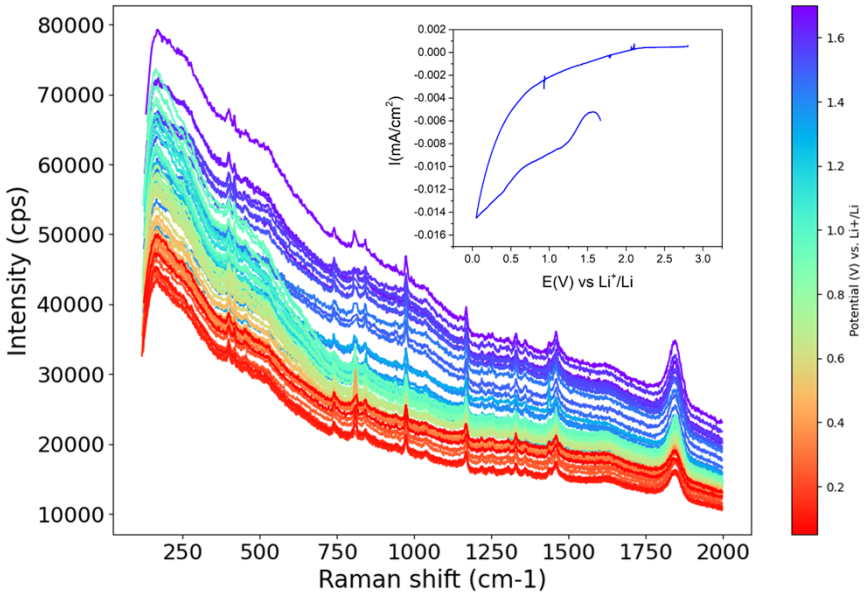

Fig. S7 Raman *operando* of the 1M LiTFSI in TEGDME electrolyte on polypropylene Celgard separator and its voltammogram obtained at 0.03 $mV.s^{-1}$