Supplementary Information for

$K_2Fe_4O_7$ superionic conductor for high-rate all-solid-state potassium metal batteries

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Table S1. Crystal data and structure refinement for $K_2Fe_4O_7$.

Empirical formula	$K_2Fe_4O_7$
Formula weight	413.60
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Trigonal, P-31m
Unit cell dimensions	a = 5.155(5) Å α = 90º
	b = 5.155(5) Å β = 90º
	c = 6.902(13) Å γ = 120º
Volume	158.9(4) $Å^3$
Z, Calculated density	1, 4.323 Mg/m^3
Absorption coefficient	10.252 mm^{-1}
F(000)	198
Crystal size	0.15 x 0.12 x 0.11 mm
Theta range for data collection	2.95 to 30.85 º
Limiting indices	$-7 \leq h \leq 6$, $-4 \leq k \leq 7$, $-9 \leq l \leq 8$
Reflections collected / unique	1060 / 198 [R(int) = 0.0202]
Completeness to theta = 30.85	97.1 %
Absorption correction	Empirical
Max. and min. transmission	0.3318 and 0.2357
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	198 / 0 / 21
Goodness-of-fit on F^2	1.125

Final R indices [I>2σ(I)]	R1 = 0.0327, wR2 = 0.1211
R indices (all data)	R1 = 0.0330, wR2 = 0.1214
Largest diff. peak and hole	0.808 and -1.335 e. Å $^{-3}$

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $K_2Fe_4O_7$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	6667	3333	5000	8(1)
Fe(2)	0	0	2669(2)	7(1)
K(1)	6667	3333	0	24(1)
K(1')	8140(30)	4069(15)	0	25(3)
O(1)	3505(6)	3502(6)	3374(4)	10(1)
O(2)	0	0	0	14(1)

Table S3. Bond lengths [Å] and angles [º] for $K_2Fe_4O_7$.

Fe(1)-O(1)#1	2.018(3)	Fe(1)-O(1)#2	2.018(3)
Fe(1)-O(1)#3	2.018(3)	Fe(1)-O(1)#4	2.018(3)
Fe(1)-O(1)	2.018(3)	Fe(1)-O(1)#5	2.018(3)
Fe(2)-O(2)	1.842(4)	Fe(2)-O(1)	1.870(3)
Fe(2)-O(1)#9	1.870(3)	Fe(2)-O(1)#10	1.870(3)
O(1)-Fe(1)#5	2.018(3)	O(2)-Fe(2)#27	1.842(4)

O(1)#1-Fe(1)-O(1)#2	91.09(18)
O(1)#1-Fe(1)-O(1)#3	84.94(14)
O(1)#2-Fe(1)-O(1)#3	92.06(12)
O(1)#1-Fe(1)-O(1)#4	92.06(12)
O(1)#2-Fe(1)-O(1)#4	84.94(14)
O(1)#3-Fe(1)-O(1)#4	175.73(14)
O(1)#1-Fe(1)-O(1)	175.73(15)
O(1)#2-Fe(1)-O(1)	92.06(12)
O(1)#3-Fe(1)-O(1)	92.06(12)
O(1)#4-Fe(1)-O(1)	91.09(18)
O(1)#1-Fe(1)-O(1)#5	92.06(12)
O(1)#2-Fe(1)-O(1)#5	175.73(15)
O(1)#3-Fe(1)-O(1)#5	91.09(18)
O(1)#4-Fe(1)-O(1)#5	92.06(12)
O(1)-Fe(1)-O(1)#5	84.94(14)
O(2)-Fe(2)-O(1)	105.10(9)
O(2)-Fe(2)-O(1)#9	105.10(9)
O(1)-Fe(2)-O(1)#9	113.47(8)
O(2)-Fe(2)-O(1)#10	105.10(9)
O(1)-Fe(2)-O(1)#10	113.47(8)
O(1)#9-Fe(2)-O(1)#10	113.47(8)

Fe(2)-O(1)-Fe(1)#5	120.96(10)
Fe(2)-O(1)-Fe(1)	120.96(10)
Fe(1)#5-O(1)-Fe(1)	95.06(14)
Fe(2)#27-O(2)-Fe(2)	180.0

Symmetry transformations used to generate equivalent atoms:

#1 x-y+1,x,-z+1	#2 -y+1,x-y,z	#3 -x+y+1,-x+1,z	#4 y,-x+y,-z+1
#5 -x+1,-y+1,-z+1	#6 -x+1,-y,-z+1	#7 -x+2,-y+1,-z+1	#8 x,y,z+1
#9 -y,x-y,z	#10 -x+y,-x,z	#11 -y,x-y-1,z	#12 x-y-1,x-1,-z
#13 -x+1,-y,-z	#14 y,-x+y+1,-z	#15 y-1,-x+y,-z	#16 x-1,y,z
#17 x-1,y-1,z	#18 y,-x+y,-z	#19 x-y+1,x,-z	#20 -x+1,-y+1,-z
#21 -x+2,-y+1,-z	#22 x+1,y,z	#23 x+1,y+1,z	#24 x-y,x-1,-z
#25 y+1,-x+y+1,-z	#26 x-y,x,-z	#27 -x,-y,-z	

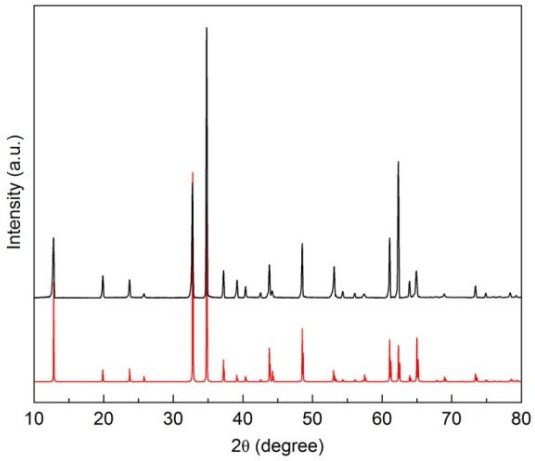

Figure S1. Single crystal simulated (red) and powder (black) XRD patterns of $K_2Fe_4O_7$.

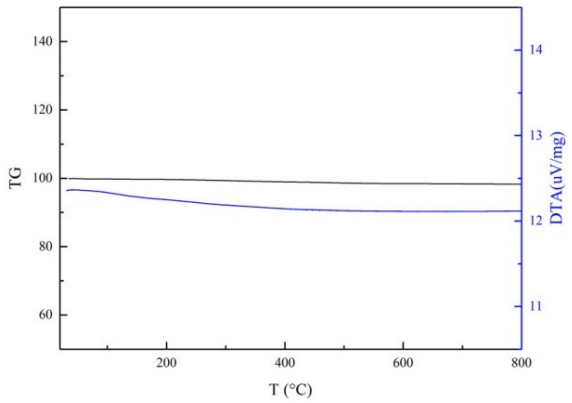

Figure S2. TG and DTA curves for $K_2Fe_4O_7$ in the temperature range of 27 – 800 ℃.

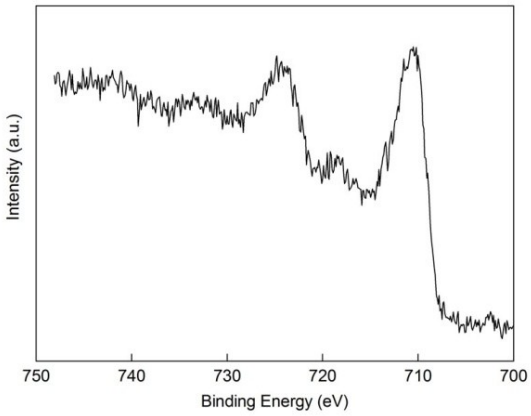

Figure S3. XPS spectrum of Fe 2p for $K_2Fe_4O_7$.

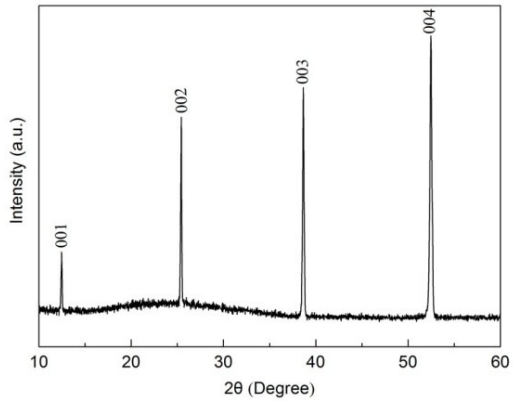

Figure S4. The X-ray angle was scanned from 10 to 60º relative to the upper plane of the single crystals

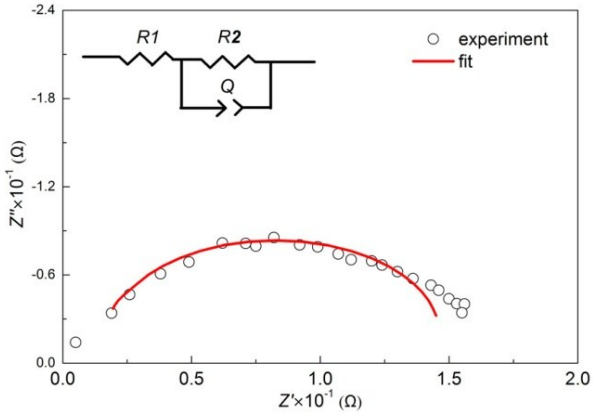

Figure S5. The equivalent circuit and an example of fit to impedance data measured along the *a*-axis at 500 ℃.