Supporting Information

Synergistic Pinning Effect in Layer-structured Oxide Cathode for Enhancing Stability towards Potassium-Ion Batteries

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KEYWORDS

Potassium ion battery; layer-structured oxide; cathode materials; structural stability; phase transformation

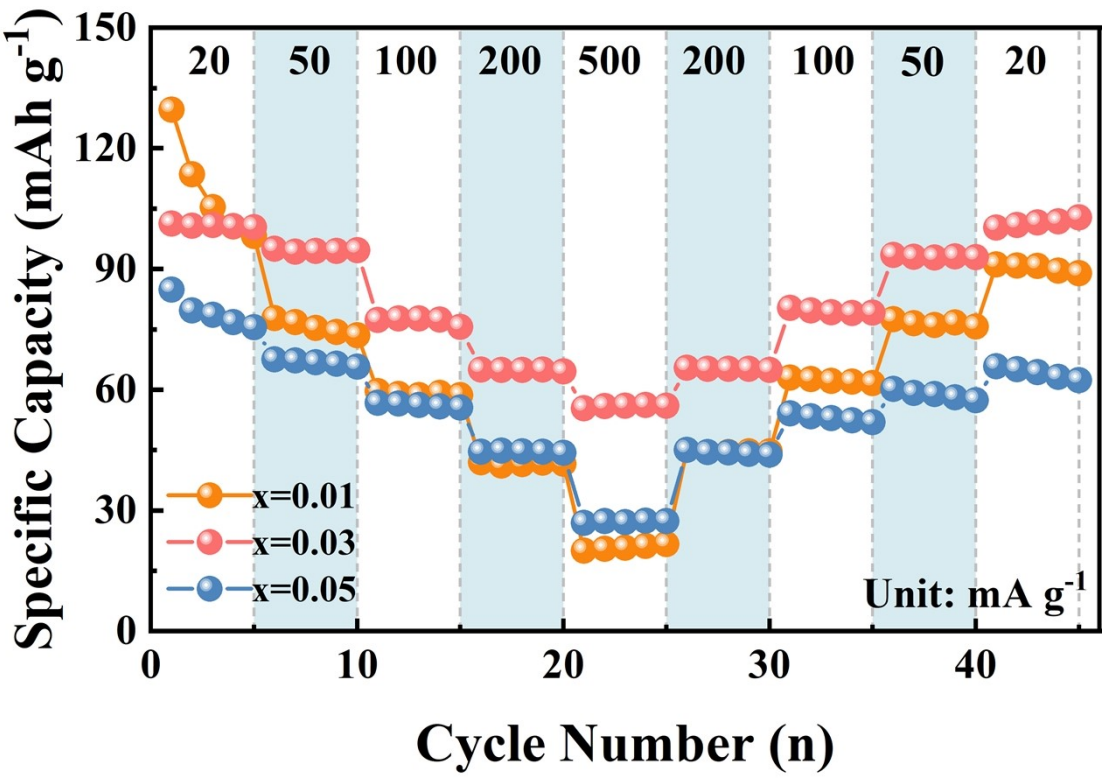

Figure S1. Rate performance comparison of $K_{0.5}Mn_{0.9-x}Co_{0.05}Fe_{0.05}Li_xO_2$ (x = 0.01, 0.03, 0.05).

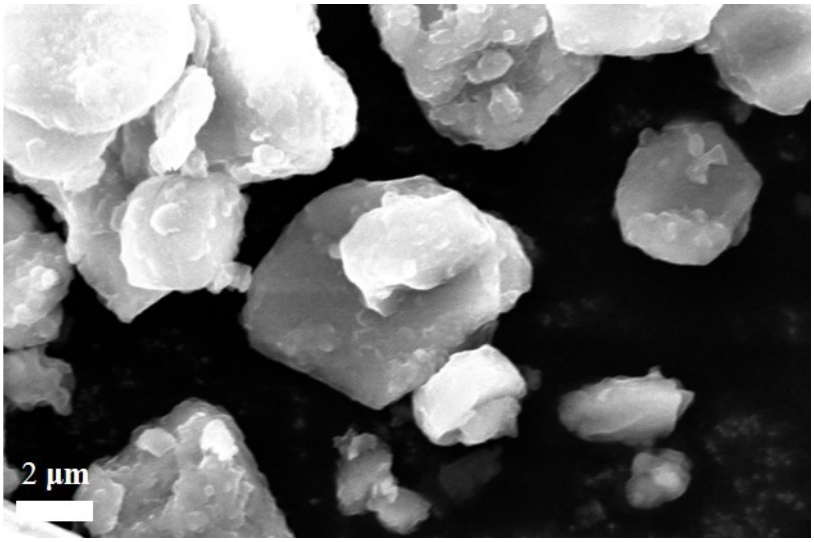

Figure S2. SEM image of KMCFO.

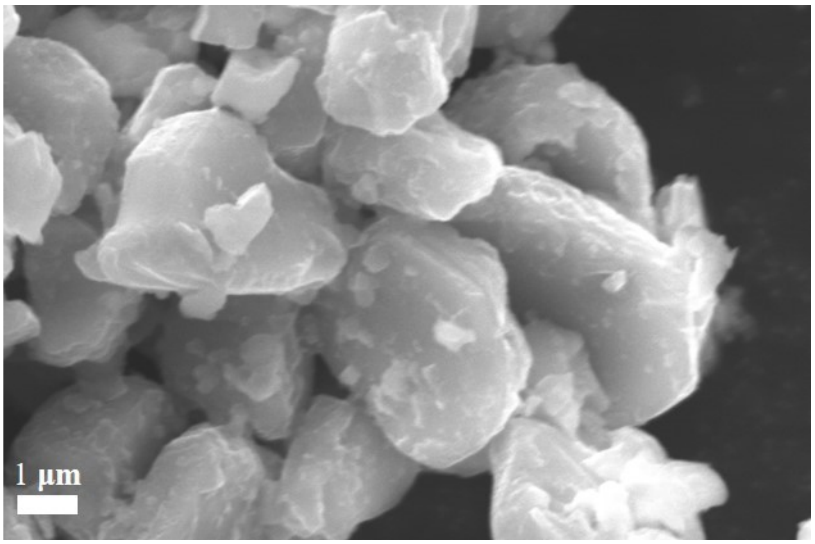

Figure S3. SEM image of KMCFLO.

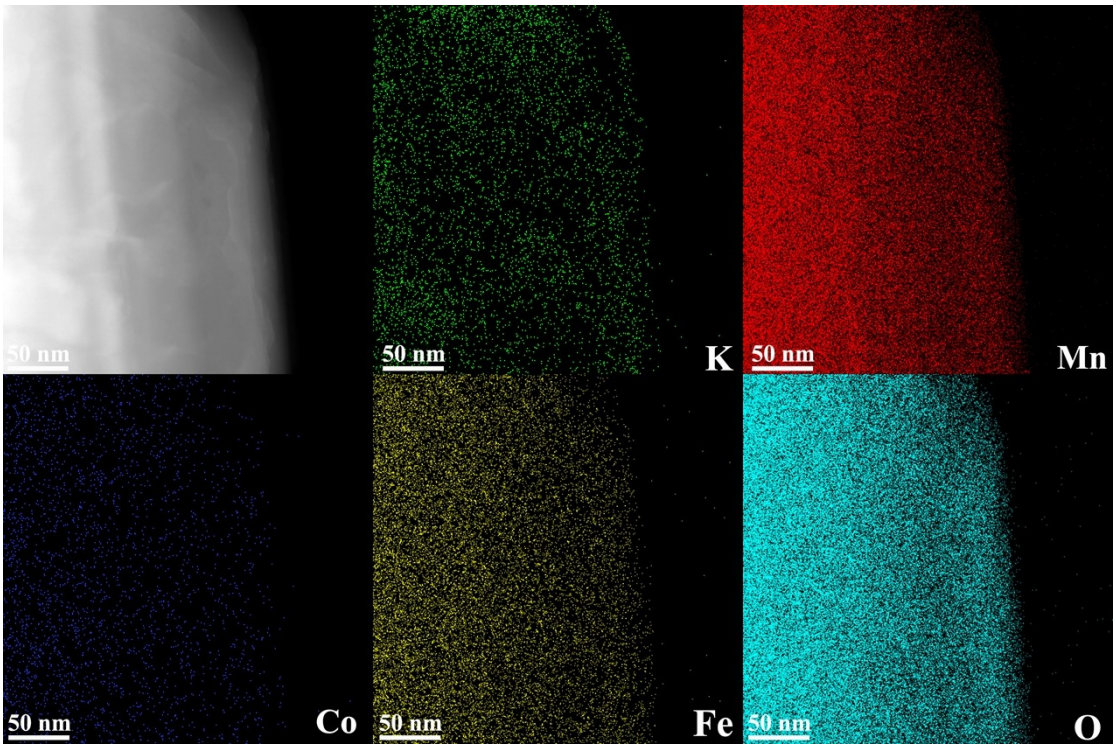

Figure S4. TEM image and the corresponding EDS mapping of the KMCFLO.

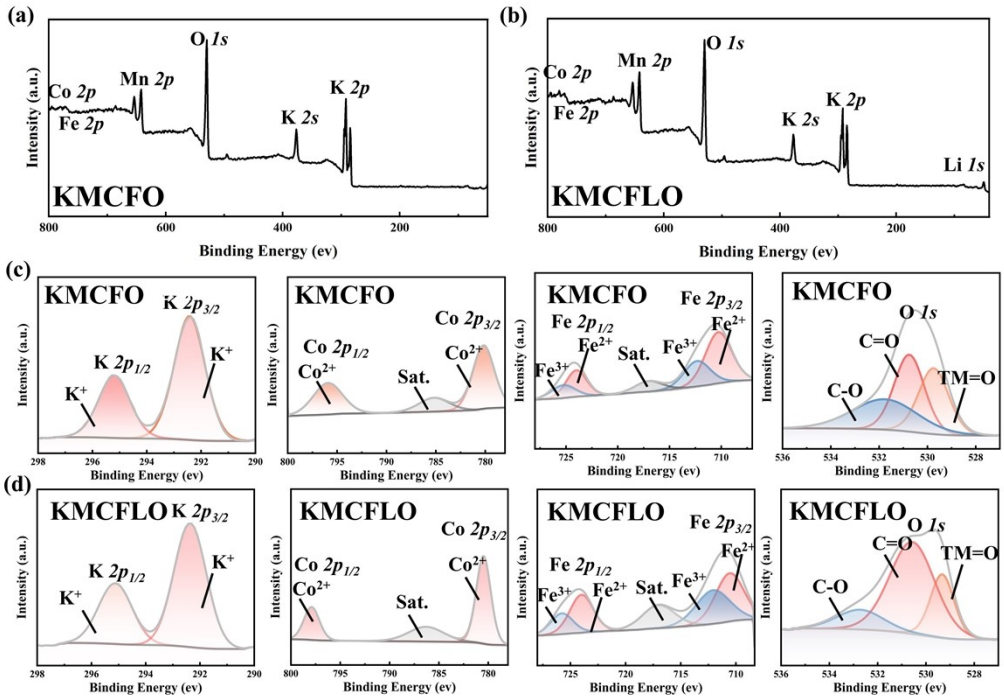

Figure S5. XPS spectra and fitting results: survey spectra of a) KMCFO and b) KMCFLO, c) K *2p*, Co *2p*, Fe *2p* and O *1s* of KMCFO, d) K *2p*, Co *2p*, Fe *2p* and O *1s* of KMCFLO.

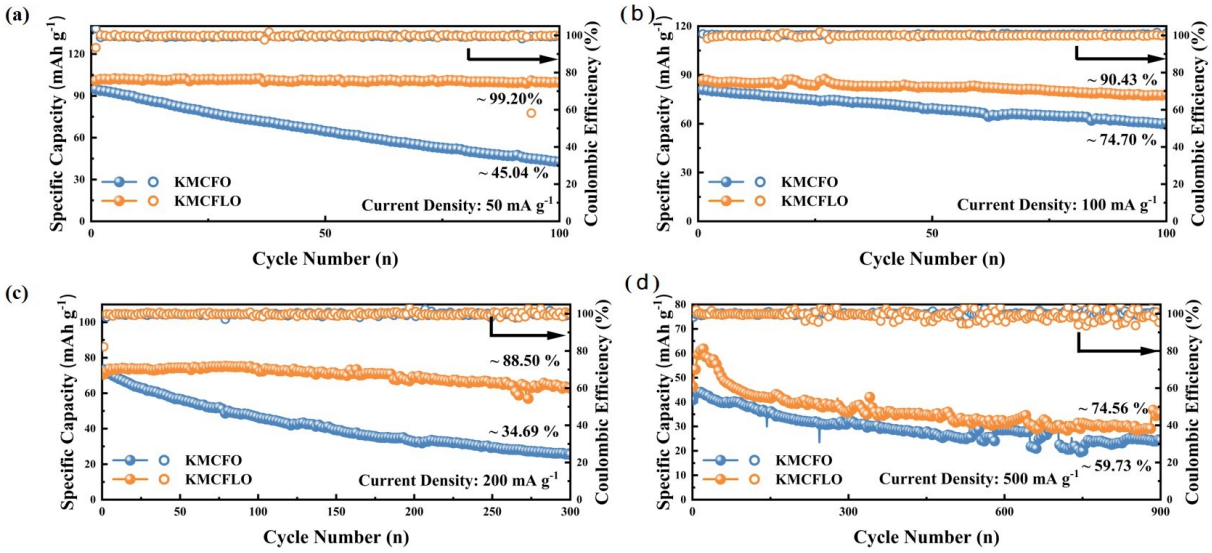

Figure S6. Long-term cycling performance of KMCFO and KMCFLO at a)50 mA g^{-1}, b) 100 mA g^{-1}, c) 200 mA g^{-1}, d) 500 mA g^{-1}.

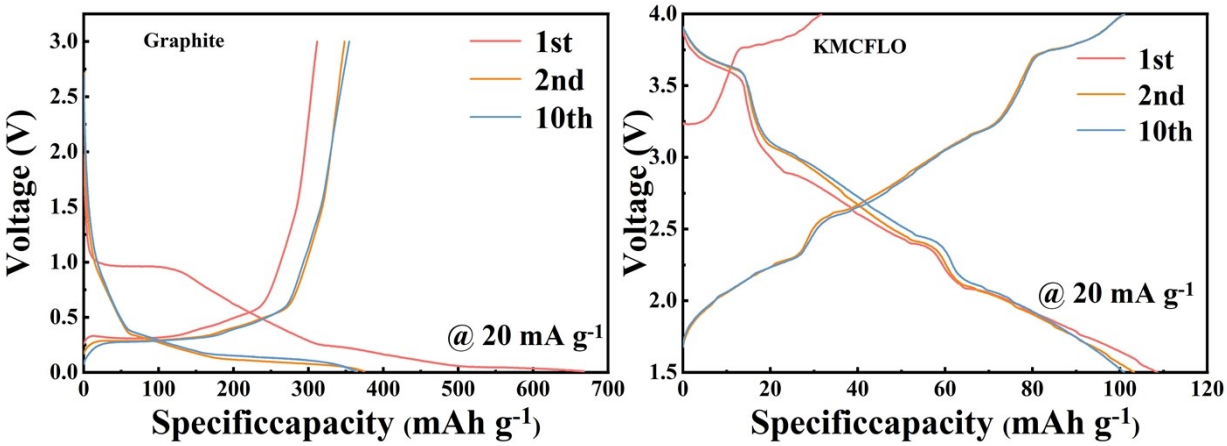

Figure S7. Electrochemical performance of KMCFLO and graphite electrodes in half-cells.

Table S1. Structural parameters of KMCFO and KMCFLO obtained by Rietveld refinement of Figure 1a.

	a-axis (Å)	c-axis (Å)	R_{wp} (%)	GOF	Space group	ICDD-PDF	Wt%
KMCFO	2.827	20.999	3.85	4.38	R 3 m	16-0205	—
KMCFLO	2.886	20.886	7.984	5.78	R 3 m	16-0205	95.1 %
	4.929	8.5305			C 2/c	27-1252	4.9%

Table S2. Information of the fitting procedure for XPS test results of powder samples.

Samples and Current Density (mA g^{-1})		Initial Specific Discharge Capacity (mAh g^{-1})	Number of Cycles (n)	Capacity Retention (%)
KMCFO	20	103.8	100	68.04
	50	94.7	100	45.04
	100	80.8	100	74.70
	200	73.3	300	34.69
	500	40.8	900	59.73
KMCFLO	20	107.1	100	82.36
	50	100.8	100	99.20
	100	86.8	100	90.43
	200	70.6	300	88.50
	500	46.3	900	74.56

Table S3. Information of the fitting procedure for XPS test results of powder samples.

Samples and Elemental Orbits		Position Constraint (eV)	FWHM Constraint (eV)	Residual Standard Deviation
KMCFLO	K *2p*	Δ_K=2.8	0.5-2.0	3.01
	Mn *2p*	Δ_{Mn}=11.2	0.5-3.0	1.753
	Co *2p*	Δ_{Co}=14.99	0.5-2.0	1.21
	Fe *2p*	Δ_{Fe}=13.1	0.5-3.0	1.19
	Li *1s*	/	0.5-2.5	1.283
	O *1s*	/	0.5-2.5	1.348
KMCFO	K *2p*	Δ_K=2.8	0.5-2.0	2.147
	Mn *2p*	Δ_{Mn}=11.2	0.5-3.0	1.302
	Co *2p*	Δ_{Co}=14.99	0.5-2.0	1.005

Fe *2p*	Δ_{Fe}=13.1	0.5-3.0	1.136
O *1s*	/	0.5-2.5	0.8965

Table S4. The information on the split fitting peak of XPS tests for Fe *2p*, Co *2p*, K *2p* and O *1s* in KMCFO and KMCFLO materials.

Samples and Elemental Orbits		Peak Position of the Fitting Peak (eV)	FWHM Constraint (eV)
KMCFO	K $2p_{1/2}$	295.19	0.5-2.0
	K $2p_{3/2}$	294.42	0.5-2.0
	Co $2p_{1/2}$	795.93	0.5-2.0
	Co $2p_{3/2}$	780.18	0.5-2.0
	Fe $2p_{1/2}$	724.00, 725.26	0.5-3.0
	Fe $2p_{3/2}$	710.28, 712.33	0.5-3.0
	O *1s*	529.70, 530.75, 531.75	0.5-2.5
KMCFLO	K $2p_{1/2}$	295.12	0.5-2.0
	K $2p_{3/2}$	292.36	0.5-2.0
	Co $2p_{1/2}$	795.17	0.5-2.0
	Co $2p_{3/2}$	780.14	0.5-2.0
	Fe $2p_{1/2}$	723.99, 725.78	0.5-3.0
	Fe $2p_{1/2}$	710.55, 712.07	0.5-3.0
	O *1s*	529.3, 530.57, 532.72	0.5-2.5

Table S5. The comparison of electrochemical performances between some reported cathode materials and KMCFLO in this work.

Cathode	Method	Voltage range	Capacity	Capacity retention
$K_{0.32}MnO_2$	hydrothermal	2.0-4.5V	28.8 mA h g^{-1} at 500 mA g^{-1}	73.37% at 100 mA g^{-1} (100 cycles)
$K_{0.44}Ni_{0.22}Mn_{0.78}O_2$	solid-state	1.5-4.0V	58 mA h g^{-1} at 500 mA g^{-1}	67% at 200 mA g^{-1} (500 cycles)
$K_{0.3}Mn_{0.95}Co_{0.05}O_2$	sol-gel	2.0-3.6V	99 mA h g^{-1} at 22 mA g^{-1}	75% at 173 mA g^{-1} (500 cycles)
$K_{0.6}CoO_2$	solvent-thermal	1.7-4.0 V	40 mA h g^{-1} at 200 mA g^{-1}	87% at 40 mA g^{-1} (300 cycles)
$KCrO_2$	solid-state	1.5-4.0 V	31 mA h g^{-1} at 500 mA g^{-1}	67% at 10 mA g^{-1} (100 cycles)
$K_{0.5}MnO_2@Al_2O_3$	solvothermal	1.5-4.0 V	95.3 mA h g^{-1} at 50 mA g^{-1}	53% at 50 mA g^{-1} (300 cycles)
$K_{0.54}Mn_{0.78}Mg_{0.22}O_2$	solid-state	1.5-4.0 V	96.8 mA h g^{-1} at 100 mA g^{-1}	84% at 100 mA g^{-1} (100 cycles)
$K_{0.5}Mn_{0.9}Mg_{0.1}O_2$	solid-state	1.5-4.0 V	102 mA h g^{-1} at 10 mA g^{-1}	21.5% at 100 mA g^{-1} (400 cycles)

Table S6. Fitting results of variable temperature electrochemical impedance spectroscopy and apparent activation energy magnitude.

Sample	Temperature (℃)	R_{ct} (Ω)	E_a (KJ mol^{-1})
KMCFO	10	37930	84.04
	15	21786	
	20	12844	
	25	7540	
	30	4506	
KMCFLO	10	26746	81.55
	15	15734	
	20	8940	
	25	5614	
	30	3207	

Table S7. The peak current at different scan rates and calculation results of D_k.

Sample	Position	Peak current (mA, follow the scan rates of 0.2, 0.5, 1, 2, 5 mV s^{-1}, the '-' for discharge)	Slope of the fitting curve	D_k (cm^2 s^{-1}, '-' for discharge)
KMCFO	Peak 1	0.024, 0.057, 0.133, 0.206, 0.449	0.246	4.49×10^{-10}
	Peak 2	-0.027, -0.058, -0.090, -0.143, -0.254	-0.127	-2.32×10^{-10}
	Peak 3	-0.024, -0.062, -0.098, -0.181, -0.379	-0.126	-2.30×10^{-10}
KMCFLO	Peak 1	0.028, 0.071, 0.147, 0.265, 0.581	0.312	5.70×10^{-10}
	Peak 2	-0.036, -0.071, -0.118, -0.219, -0.424	-0.220	-4.02×10^{-10}
	Peak 3	-0.043, -0.100, -0.172, -0.301, -0.621	-0.300	-5.48×10^{-10}