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Figure S1 Demonstration of structural changes from KMnF₃ to MnF₃ Optimization of synthesis conditions and structure and morphology of KMnF₃



Figure S2 SEM images of KMnF₃ prepared in mixed solvents with different ratios of water and ethanol (a, b-2:1, c,d-2:1, e,f-1:2)



Figure S3 XRD and SEM image of KMnF₃ prepared by rapid pouring



Figure S4 HRTEM analysis of the KMnF₃ material



Figure S5 Discharge/charge profiles of of $KMnF_3$ cathode at the current density of 40 mA·g⁻¹ over the voltage range of 4.2–1.2V vs. K⁺/K



Figure S6 a)XRD patterns of the cathoode at different voltages during the first charge. b)

XPS spectrum of electrode pad after the first charge

electrode	The highest working voltage/ V vs K ⁺ /K
$K_{0.3}MnO_2^{17}$	3.9
$K_{0.5}MnO_2^{18}$	4.0
this work	4.2

Table S1 Comparison of potentials of manganese-based electrode materials in KIBS



Figure S7 EIS with different self-discharge time



Figure S8 Comparison of XPS test of electrode pad before and after etching



Figure S9 Comparison of EIS of KMnF₃ electrodes synthesized under optimal conditions and rapid tidings conditions after the initial charge and discharge process

Table S2 ICP-OES test results of the manganese content in the electrolyte after the first cycle of charge and discharge of the KMnF₃ electrode synthesized under the optimal conditions and rapid titration conditions.

electrode	The concentration of manganese ions in the electrolyte/mg L ⁻¹
KMnF ₃ synthesized under optimized conditions	0.023
KMnF ₃ synthesized under fast titration conditions	0.041