

## Supporting Information

### Iron-Based Fluorides of Tetragonal Tungsten Bronze Structure as Potential Cathodes for Na-Ion Batteries

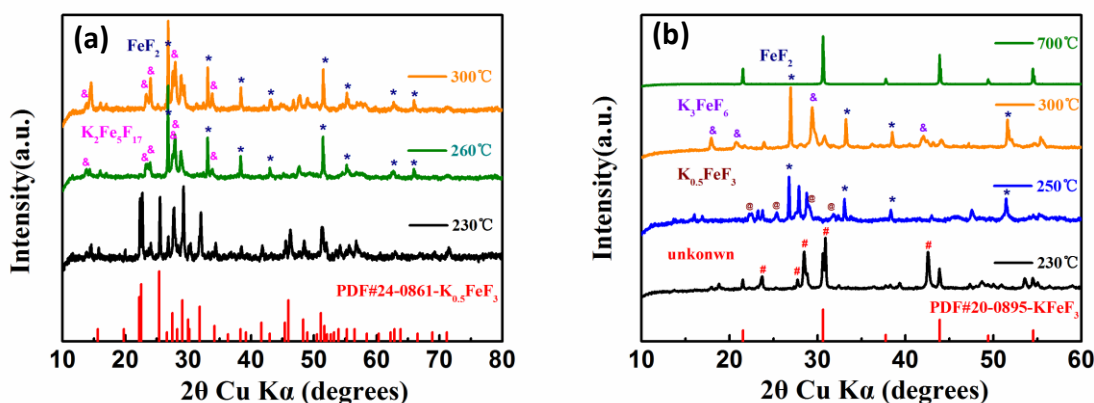
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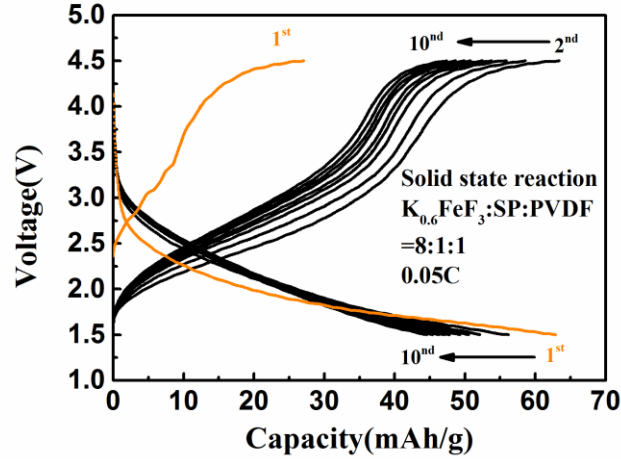
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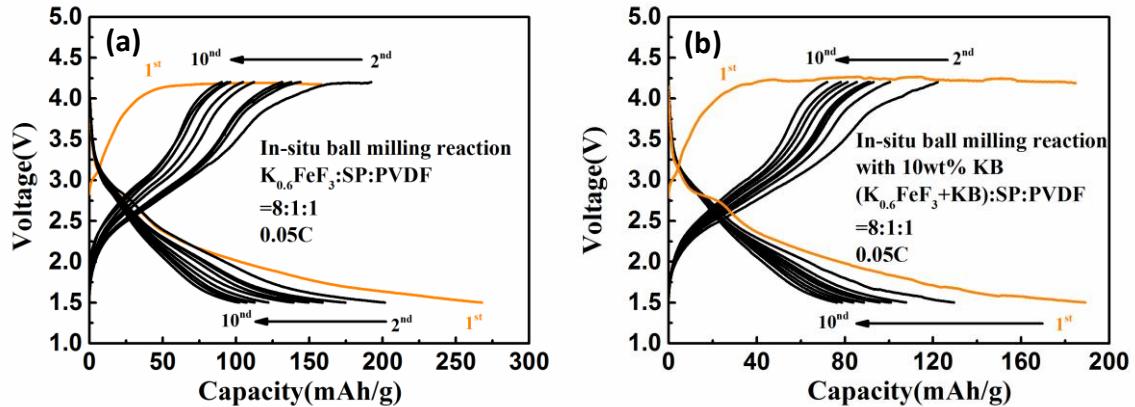
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**Figure S1.** XRD patterns of (a)  $K_{0.5}FeF_3$  prepared by solid state reaction at 230°C (black) and other products appearing at higher reaction temperatures (260°C in green and 300°C in orange), (b)  $KFeF_3$  prepared by solid state reaction at 700°C (green) and other products appearing at other lower sintering temperatures (230°C in black, 250°C in blue and 300°C in orange). The standard patterns of  $K_{0.6}FeF_3$  and  $KFeF_3$  are also listed as references.

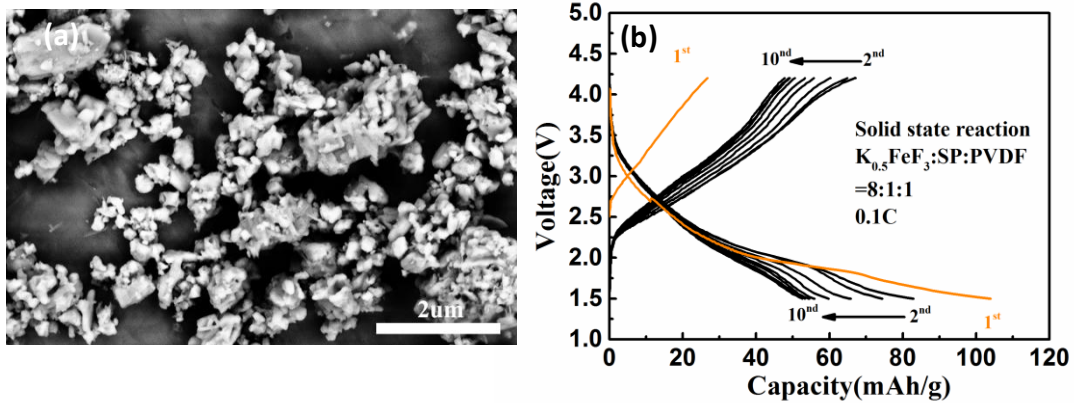


**Figure S2.** Galvanostatic charge/discharge curves of as-sintered  $K_{0.6}FeF_3$  as NIB cathodes at 0.05C with a electrode component ratio of 8:1:1 in mass according to  $K_{0.6}FeF_3$ : SP: PVDF. The initial charge capacity is highly dependent on carbon additive content, and it is less than 30 mAh/g when SP content is 10 wt% even at a lower rate of 0.05 C. It indicates that K extraction is activated by enhanced electron conductivity of composite electrode.

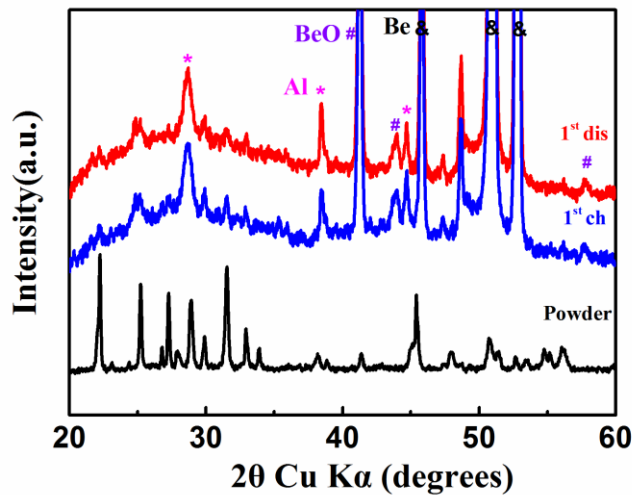


**Figure S3.** Galvanostatic charge/discharge curves of (a)  $K_{0.6}FeF_3$  and (b)  $K_{0.6}FeF_3$ -KB (10 wt%) prepared by in-situ mechanochemical method as NIB cathodes at 0.05C in a voltage range of 1.5-4.2 V. The electrode component ratio is 8:1:1 in mass according to  $K_{0.6}FeF_3$  (or  $K_{0.6}FeF_3$ -KB): SP: PVDF. Their performance is overall inferior to the materials by solid state synthesis even at a lower rate of 0.05C either due to their larger grains or to more impurities (or unreacted species). The latter is likely responsible for the unsuccessful charge exceeding 4.2 V. This results in a fast fading of capacity, which is below 100 mAh/g after 10 cycles. The addition of KB even has a negative effect on the reversible capacity, as it seems to trigger more

serious side reactions during mechanical milling with less yield of electroactive  $K_{0.6}FeF_3$ .



**Figure S4.** SEM image of pristine  $K_{0.5}FeF_3$  prepared by solid state reaction, consisting of less defined grains with visible aggregation. (b) Galvanostatic charge/discharge curves of as-sintered  $K_{0.5}FeF_3$  as NIB cathodes at 0.1C with a electrode component ratio of 8:1:1 in mass according to  $K_{0.5}FeF_3$ : SP: PVDF, showing similar electrochemical profiles with comparable capacity as  $K_{0.6}FeF_3$ .



**Figure S5.** Ex-situ XRD patterns of as-sintered  $K_{0.6}FeF_3$  powder and electrodes charged to 4.5 V and discharged to 1.5 V during the first cycle. The cycled electrodes show similar diffraction peaks as pristine powder without remarkable position shift, indicating the prior K-extraction and following sodiation occurring in a solid-solution manner with negligible change of lattice parameters and cell volume. The near-zero strain characteristic benefits from the robust open framework of TTB phase pre-supported by larger-sized K-ions.