Supporting Information

Dehydrating Bronze Iron Fluoride as High Capacity Conversion Cathode for Lithium Batteries

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Figure S1. SEM images of HTB2 wired by 5 wt% SWNTs with different scales. When using BmimBF₄ instead of C_{10} mimBF₄ as reaction medium, the grain growth of HTB2 is significantly suppressed due to potential IL coating on fluoride surface. The small grains are linked by few SWNTs for better intergrain electron transfer.



Figure S2. SEM images of HTB3 wired by 10 wt% SWNTs with different scales. When displacing $FeCl_3 \cdot 6H_2O$ by $FeF_3 \cdot 3H_2O$ as Fe precursor, the synthesis mechanism is converted to a solid-solid topotactic transformation in a top-down way. The grains of HTB3 may be large even in a size of several micrometers highly depending on the original size of precursor grains. HTB3 is less dense and porous inside its grains, which usually consist of numerous smaller particles.



Figure S3. Magnified SEM images of SWNT-wired (a) HTB-FeF₃ and (b) HTB3 samples with the same scale. The higher magnification makes their surface situation clearer. The less conductivity of fluoride and IL-species coverage on CNT and fluoride surfaces (bright regions) should be responsible for the identification difficulty to a certain degree. HTB-FeF₃ appears to be more dense and less porous than HTB3.



Figure S4. XPS spectra of (a) Fe 2p, (b) N 1s and (c) B 1s for HTB-FeF₃, HTB2 and HTB3 samples. HTB-FeF3 and HTB3 show stronger XPS peaks of Fe 2p, indicating cleaner surface with fewer IL component coating. However complete removal of surface IL components for HTB-FeF3 and HTB3 appears to be difficult since the signals of N 1s and B 1s denoting N-C and B-F binding respectively are comparable. The Cl 2p signals are even observed for the ionothermal samples.



Figure S5. (a) Galvanostatic charge/discharge curves of HTB-FeF₃ as insertion cathode in a voltage range of 1.7-4.5 V after electrochemical activation by the initial conversion reaction at different rates from 0.1 C to 1 C. (b) Corresponding discharge capacity of HTB-FeF₃ as a function of cycle number. The HTB phase is amorphized after electrochemical activation and able to release a reversible insertion capacity of 200, 112 and 76 mAh/g at 0.1C, 0.5C and 1C respectively.



Figure S6. Galvanostatic charge/discharge curves of (a) HTB2 and (b) HTB3 as conversion cathodes in a voltage range of 1.3-4.5 V during the first ten cycles at 0.1 C. In this wider voltage range from 1.3 V to 4.5 V, the insertion-conversion capacity of first discharge is about 550 mAh/g and 420 mAh/g for HTB2 and HTB3 respectively. Their first charge capacities are less reversible than for HTB-FeF₃, indicating a lower initial coulombic efficiency (CE). The following discharge capacity is maintained at ~250 mAh/g after 10 cycles. The capacity degradation mainly stems from the lower conversion region, whereas the upper insertion region is better preserved. Thick conformal coating of insulative IL would interrupt smooth electron transfer, therefore leading to a poorer CE as well as a lower transition voltage (1.3 V) from insertion region to conversion one for HTB2. The hydration status of HTB2 and HTB3 is also indicated from the unreachable theoretical insertion capacity (actually < 200 mAh/g).