Electronic Supplementary Information

Engineering doping-vacancy double defects and insights into the conversion mechanisms of an Mn-O-F ultrafine nanowire anode for enhanced Li/Na-ion storage and hybrid capacitors

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Table of Contents

Experimental

Scheme S1  Schematics of the process for the formation of Mn-O-F ultrafine nanowires.

Figure S1  The crystal structures of tetragonal MnF$_2$ (A) and defective MnF$_2$-E (B) and detailed crystalline parameters for tetragonal MnF$_2$ (C).

Figure S2  XRD patterns of MnF$_2$ 1-9#.

Figure S3  SEM (A)/TEM (B) images of MnF$_2$ 8#-E sample.

Figure S4  A picture of MnF$_2$ 8# and MnF$_2$ 8#-E samples.

Figure S5  EDS spectra of MnF$_2$ 8# (A) and MnF$_2$ 8#-E (B) samples.

Figure S6  Specific capacity and Coulombic efficiency derived from the respective 5$^{th}$ cycle at 0.1-3.2 A g$^{-1}$ of MnF$_2$ 1#-9# electrodes (A); cycling stability for 500 cycles at 2 A g$^{-1}$ of MnF$_2$ 1#-9# electrodes (B).

Figure S7  CV plots of the first three cycles of MnF$_2$ 1#-9# electrodes at 0.3 mV s$^{-1}$.

Figure S8  GCD curves of the first five cycles for MnF$_2$ (1#, 2#, 3#, 4#, 5#, 6#, 7#, 9#) electrodes at 0.1 A g$^{-1}$.

Figure S9  GCD curves of MnF$_2$ 1#-6# electrodes at 0.1-3.2 A g$^{-1}$.

Figure S10  GCD curves of MnF$_2$ 7#-9# and MnF$_2$ 8#-E electrodes at 0.1-3.2 A g$^{-1}$.

Figure S11  Rate performance and Coulombic efficiency of MnF$_2$ 1#-6# electrodes at 0.1-3.2-0.1 A g$^{-1}$.

Figure S12  Rate performance and Coulombic efficiency of MnF$_2$ 7#-9# and MnF$_2$ 8#-E electrodes at 0.1-3.2-0.1 A g$^{-1}$.

Figure S13  Cycling stability and Coulombic efficiency of MnF$_2$ 1#-6# electrodes at 2 A g$^{-1}$ for 500 cycles.

Figure S14  Cycling stability and Coulombic efficiency of MnF$_2$ 7#-9# and MnF$_2$ 8#-E electrodes at 2 A g$^{-1}$ for 500 cycles.

Figure S15  XRD patterns and TEM images of the MnF$_2$ 8# (A, C, E) and MnF$_2$ 8#-E (B, D, F) electrodes after the cycling for Li-ion storage.

Figure S16  The pseudocapacitive contributions (the shaded region) of the MnF$_2$ 8# electrode at 0.1-0.3 mV s$^{-1}$ (a-c) and the contribution ratios (d) for Li-ion storage.

Figure S17  The pseudocapacitive contributions (the shaded region) of the MnF$_2$ 8#-E electrode at 0.1-0.3 mV s$^{-1}$ (a-c) and the contribution ratios (d) for Li-ion storage.
Figure S18 The equivalent circuit model of Nyquist plots for MnF$_2$ and MnF$_2$ 8#-E electrodes.

Figure S19 Nyquist plots of MnF$_2$ and MnF$_2$ 8#-E electrodes (the insets are the enlarged high frequency regions).

Figure S20 GCD curves of MnF$_2$ 8# (A) and MnF$_2$ 8#-E (B) electrodes at the precharged current density of 0.1 A g$^{-1}$.

Figure S21 Performance of AC electrode for Li-ion storage.

Figure S22 CV plots at 40 mV s$^{-1}$ (A), GCD curves at 1 A g$^{-1}$ (B), Ragone plots (C) and cycling behavior for 5000 cycles at 5 A g$^{-1}$ (D) of 4.5 V-MnF$_2$//AC LICs (1:1) and 4.6 V-MnF$_2$//AC LICs (1:2).

Figure S23 The third cycle of CV curves under 0-5 V at 1 mV s$^{-1}$: MnF$_2$//AC LICs (1:1) (A), MnF$_2$//AC LICs (1:2) (B).

Figure S24 CV plots of 4.5 V-MnF$_2$//AC LICs (1:1) at 10-160 mV s$^{-1}$ (A), GCD curves of 4.5 V-MnF$_2$//AC LICs (1:1) at 0.5-16 A g$^{-1}$ (B), CV plots of 4.6 V-MnF$_2$//AC LICs (1:2) at 10-160 mV s$^{-1}$ (C), GCD curves of 4.6 V-MnF$_2$//AC LICs (1:2) at 0.5-16 A g$^{-1}$ (D).

Figure S25 CV plots at 40 mV s$^{-1}$ (A), GCD curves at 1 A g$^{-1}$ (B), Ragone plots (C) and cycling behavior for 5000 cycles at 5 A g$^{-1}$ (D) of 4 V-MnF$_2$//AC LICs (1:1), (1:2) and (1:3).

Figure S26 CV plots of 4 V-MnF$_2$-E//AC LICs (1:1) (A), 4 V-MnF$_2$-E//AC LICs (1:2) (C) and 4 V-MnF$_2$-E//AC LICs (1:3) (E) at 10-160 mV s$^{-1}$, GCD curves of 4 V-MnF$_2$-E//AC LICs (1:1) (B), 4 V-MnF$_2$-E//AC LICs (1:2) (D) and 4 V-MnF$_2$-E//AC LICs (1:3) (F) at 0.5-16 A g$^{-1}$.

Figure S27 CV plots of 4 V-MnF$_2$//AC LICs (1:1) (A) and 4.3 V-MnF$_2$//AC LICs (1:1) (C) at 10-160 mV s$^{-1}$, GCD curves of 4 V-MnF$_2$//AC LICs (1:1) (B) and 4.3 V-MnF$_2$//AC LICs (1:1) (D) at 0.5-16 A g$^{-1}$.

Figure S28 CV plots of 4.3 V-MnF$_2$-E//AC LICs (1:2) (A), GCD curves of 4.3 V-MnF$_2$-E//AC LICs (1:2) (B) at 0.5-16 A g$^{-1}$.

Figure S29 GCD curves of MnF$_2$ 8# (A) and MnF$_2$ 8#-E(B) at 0.1-1.6 A g$^{-1}$.

Figure S30 Rate performance and Coulombic efficiency of MnF$_2$ 8# (A) and MnF$_2$ 8#-E (B) electrodes at 0.1-1.6-0.1 A g$^{-1}$, Cycling stability and Coulombic efficiency of MnF$_2$ 8# (C) and MnF$_2$ 8#-E (D) electrodes at 0.3 A g$^{-1}$ for 500 cycles.

Figure S31 XRD patterns and TEM images of the MnF$_2$ 8# (A, C, E) and MnF$_2$ 8#-E (B, D, F) electrodes after the cycling for Na-ion storage.

Figure S32 The pseudocapacitive contributions (the shaded region) of the MnF$_2$ 8# electrode at 0.1-0.3 mV s$^{-1}$ (a-c) and the contribution ratios (d) for Na-ion storage.
Figure S33 The pseudocapacitive contributions (the shaded region) of the MnF₂ 8#-E electrode at 0.1-0.3 mV s⁻¹ (a-c) and the contribution ratios (d) for Na-ion storage.

Figure S34 Nyquist plots of MnF₂ and MnF₂ 8#-E electrodes (the insets are the enlarged high frequency regions).

Figure S35 GCD curves of MnF₂ 8# (A) and MnF₂ 8#-E (B) electrodes at the precharged current density of 0.1 A g⁻¹.

Figure S36 Performance of AC electrode for Na-ion storage.

Figure S37 CV plots at 40 mV s⁻¹ (A), GCD curves at 1 A g⁻¹ (B), Ragone plots (C) and cycling behavior for 5000 cycles at 3 A g⁻¹ (D) of 4.6 V-MnF₂//AC NICs (1:1) and 4.8 V-MnF₂//AC NICs (1:2).

Figure S38 The third cycle CV curves at 1 mV s⁻¹ under 0-5 V: MnF₂//AC NICs (1:1) (A), and MnF₂//AC NICs (1:2) (B).

Figure S39 CV plots of 4.6 V-MnF₂//AC NICs (1:1) (A) and 4.8 V-MnF₂//AC NIC (1:2) (C), at 10-160 mV s⁻¹, GCD curves of 4.6 V-MnF₂//AC NIC (1:1) (B) and 4.8 V-MnF₂//AC NICs (1:2) (D) at 0.5-8 A g⁻¹.

Figure S40 CV plots of 4 V-MnF₂//AC NICs (1:1) (A) and 4.3 V-MnF₂//AC NICs (1:1) (C), at 10-160 mV s⁻¹, GCD curves of 4 V-MnF₂//AC NICs (1:1) (B) and 4.3 V-MnF₂//AC NICs (1:1) (D) at 0.5-8 A g⁻¹.

Figure S41 CV plots of 4 V-MnF₂-E//AC NICs (1:1) (A) and 4.3 V-MnF₂-E//AC NICs (1:1) (C) at 10-160 mV s⁻¹, GCD curves of 4 V-MnF₂-E//AC NICs (1:1) (B) and 4.3 V-MnF₂-E//AC NICs (1:1) (D) at 0.5-8 A g⁻¹.

Table S1 Orthogonal experimental design.

Table S2 Synthesis condition of MnF₂ 1#-9#.

Table S3 Orthogonal experimental analysis results of MnF₂.

Table S4 Summary of performance of MnF₂ 1#-9# and MnF₂ 8#-E electrodes.

Table S5 A comparasion for Mn-O-F (MnF₂ 8#-E) anode with literature for LIBs.

Table S6 EIS parameters of MnF₂ and MnF₂ 8#-E electrodes for Li-ion storage.

Table S7 Summary of performance of MnF₂//AC and MnF₂-E//AC LICs and NICs.

Table S8 Electrochemical performance comparison for some reported LICs.

Table S9 EIS parameters of MnF₂ 8# and MnF₂ 8#-E electrodes for Na-ion storage.

Table S10 Electrochemical performance comparison for some reported NICs.

Table S11 Chemicals, agents and materials.

References
Experimental

Synthesis of materials
The MnF$_2$ materials were synthesized by one-pot solvothermal method according to the orthogonal experiment (Table S1, S2). Take the procedure of MnF$_2$ 8# for an example. The compounds of 4 mmol Mn(CH$_3$COO)$_2$•4H$_2$O and 7 mL HF (40%) were added into 30 mL ethylene glycol (EG) solvents, and the mixture was magnetically stirred thoroughly and dispersed well in an ultrasonic bath. Subsequently, the mixture was put into a 50 ml Teflon lined stainless steel reactor, which was heated at 190 °C for 6 h in an electric oven, and cooled down naturally. Then, the yielded precipitates were washed with absolute alcohol several times and collected by centrifugal filtration. Finally, the collected precipitates were dried overnight at 100 °C to obtain the ultimate products. The other eight MnF$_2$ samples were also synthesized as the procedure described above based on the specific orthogonal experiment conditions.

The Mn-O-F (MnF$_2$ 8#-E) materials were synthesized by a simple etching method as follows: 100 mg of MnF$_2$ 8# was added into 1 M NaBH$_4$ aqueous solution with continuous stirring for 1 h, next, the mixture was centrifuged with distilled water and absolute alcohol in turn for several times, and then the precipitates were placed in a drying oven at 100 °C for 12 h to obtain the Mn-O-F materials. The possible process for the formation of Mn-O-F ultrafine nanowires can be seen in the Scheme 1 (ESI) (the chemicals in the experiment can be seen in the Table S11).

Characterizations
The phases and crystallinity properties were determined by X-ray diffraction (XRD). The surface chemical compositions and electronic structures were checked by X-ray photoelectron spectra (XPS). The morphology and size of particles were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The crystalline microstructures were resolved by the high-resolution TEM (HRTEM) and selected area electron diffraction (SAED). The element composition and distribution were measured by X-Ray energy dispersive spectra (EDS) and mapping. The chemical functional groups were measured by Fourier transform infrared spectroscopy (FTIR). The specific surface area, pore volume and size distribution were examined by nitrogen isothermal sorptions with Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods.
Electrochemical measurements

The electrodes were prepared as follows: firstly, a well-dispersed mixture of 70 wt% active materials (as-synthesized MnF_2 (1#-9# and 8#-E) or commercial activated carbon (AC), 20 wt% AB conductive agent and 10 wt% polyvinylidene fluoride (PVDF) binder dissolved into the N-methyl-2-pyrrolidone (NMP)) were casted onto the current collectors (the collectors for anode and cathode are Cu foil and carbon-coated Al foil respectively, with the thickness of 15 μm), and followed by drying in a vacuum oven at 110 °C for 12 h; Secondly, the electrodes were punched into disks with diameter of 12 mm, and the mass loading of active materials was about 1-4 mg cm⁻². The electrochemical performances were examined by cyclic voltammetry (CV), galvanostatistic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) tests via CHI 660E electrochemical working stations and Neware-CT-4008 testers. Tests for Li//MnF_2 (1#-9# and 8#-E) and Li//AC or Na//MnF_2 (8# and 8#-E) and Na//AC half-cells were conducted by using the type 2032 coin cells with a MnF_2 or AC working electrode (WE), a Li or Na plate as both counter electrode (CE) and reference electrode (RE), and one piece of glass fiber (GF) as separator. Tests for MnF_2 (8# and 8#-E)//AC LICs/NICs full-cells were conducted via type 2032 coin cells, with certain active mass ratio of anode and cathode, and the MnF_2 (8# and 8#-E) anodes were precharged (pre-lithiation or pre-sodiation) at 0.1 A g⁻¹ for 3.5 cycles. The electrolytes for Li//MnF_2 (1#-9# and 8#-E) and Li//AC half-cells and MnF_2 (8# and 8#-E)//AC LICs were 1 M LiPF_6 dissolved in the mixed solvents of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1 in volume) with 1% vinylene carbonate (VC) additives (CAPCHEM); The electrolytes for Na//MnF_2 (8# and 8#-E) and Na//AC half-cells and MnF_2 (8# and 8#-E)//AC NICs were 0.85 M NaPF_6 dissolved in the mixed solvents of EC, and dimethyl carbonate (DEC) (1:1 in volume) with 5% fluoroethylene carbonate (FEC) additives (MJS). All cell assemblies were performed in an high pure Ar-filled dry glovebox (MIKROUNA, O₂ and H₂O<0.1 ppm), and all tests were carried out at room temperature (about 25 °C). The chemicals, agents and materials for electrochemical tests are listed in the Table S11. The calculations for the specific capacity (Cₘₙ, mAh g⁻¹), energy density (Eₘₙ, Wh kg⁻¹) and power density (Pₘₙ, kW kg⁻¹) are on the basis of Equations S(1), (2) and (3):

\[ C_m = \frac{Q}{3.6m} \]  \hspace{1cm} S(1)

\[ E_m = \frac{(C_m \Delta V)}{2} \]  \hspace{1cm} S(2)

\[ P_m = 3.6E_m/t \]  \hspace{1cm} S(3)

Where \( m \), \( Q \), \( \Delta V \), and \( t \) are mass of active materials (g, for LICs and NICs, it refers to the total masses of active materials of anode and cathode), charge quantity (C), voltage window (V), and discharge time (s), respectively.
**Scheme S1**  Schematics of the process for the formation of Mn-O-F ultrafine nanowires.

The possible process for the formation of Mn-O-F ultrafine nanowires can be seen in the **Scheme 1** (ESI). In the etching process by NaBH₄ solutions, the bonds among crystalline particles would be weakened and the crystals would become more porous and linear and finally form nanowire morphology under the continuous impact of H₂ flow, meanwhile, the Mn²⁺ would be partially reduced to unstable Mn⁺ in the MnF₂ nanocrystal and produce the F⁻ vacancy; during the centrifugal filtration, with the removal of the excess of NaBH₄ solutions, the unstable Mn⁺ in the MnF₂ nanocrystal would be oxidized to stable Mn²⁺ by O₂ in air and the O²⁻ would also partially occupy the position of F⁻ vacancy and finally form the Mn-O-F nanowires with the hetero oxygen doping and fluorine vacancies double defects.
Figure S1 The crystal structures of tetragonal MnF$_2$ (A) and defective MnF$_2$-E (B) and detailed crystalline parameters for tetragonal MnF$_2$ (C).
Figure S2 XRD patterns of MnF$_2$ 1-9# samples.
Figure S3  SEM (A)/TEM (B) images of MnF$_2$ 8#-E sample.
**Figure S4**  A picture of MnF$_2$ 8# and MnF$_2$ 8#-E samples.
Figure S5  EDS spectra of MnF$_2$ 8# (A) and MnF$_2$ 8#-E (B) samples.
**Figure S6**  Specific capacity and Coulombic efficiency derived from the respective 5\textsuperscript{th} cycle at 0.1-3.2 A g\textsuperscript{-1} of MnF\textsubscript{2} 1#-9# electrodes (A); cycling stability for 500 cycles at 2 A g\textsuperscript{-1} of MnF\textsubscript{2} 1#-9# electrodes (B).
Figure S7  CV plots of the first three cycles of MnF₂ 1#-9# electrodes at 0.3 mV s⁻¹.
Figure S8  GCD curves of the first five cycles for MnF$_2$ (1#, 2#, 3#, 4#, 5#, 6#, 7#, 9#) electrodes at 0.1 A g$^{-1}$. 
Figure S9  GCD curves of MnF$_2$ 1#-6# electrodes at 0.1-3.2 A g$^{-1}$. 
Figure S10  GCD curves of MnF$_2$ 7#-9# and MnF$_2$ 8#-E electrodes at 0.1-3.2 A g$^{-1}$. 
Figure S11  Rate performance and Coulombic efficiency of MnF$_2$ 1#-6# electrodes at 0.1-3.2-0.1 A g$^{-1}$. 
**Figure S12** Rate performance and Coulombic efficiency of MnF$_2$ 7#-9# and MnF$_2$ 8#-E electrodes at 0.1-3.2-0.1 A g$^{-1}$. 
Figure S13  Cycling stability and Coulombic efficiency of MnF$_2$ 1#-6# electrodes at 2 A g$^{-1}$ for 500 cycles.
Figure S14 Cycling stability and efficiency efficiency of MnF$_2$ 7#-9# and MnF$_2$ 8#-E electrodes at 2 A g$^{-1}$ for 500 cycles.
**Figure S15**  XRD patterns and TEM images of the MnF$_2$ 8# (A, C, E) and MnF$_2$ 8#-E (B, D, F) electrodes after the cycling for Li-ion storage.
Figure S16  The pseudocapacitive contributions (the shaded region) of the MnF$_2$ 8# electrode at 0.1-0.3 mV s$^{-1}$ (a-c) and the contribution ratios (d) for Li-ion storage.

Figure S17  The pseudocapacitive contributions (the shaded region) of the MnF$_2$ 8#-E electrode at 0.1-0.3 mV s$^{-1}$ (a-c) and the contribution ratios (d) for Li-ion storage.
Figure S18  The equivalent circuit model of Nyquist plots for MnF$_2$ and MnF$_2$ 8#-E electrodes.
Figure S19 Nyquist plots of MnF₂ and MnF₂ 8#-E electrodes (the insets are the enlarged high frequency regions).
Figure S20  GCD curves of MnF$_2$ 8# (A) and MnF$_2$ 8#-E (B) electrodes at the precharged current density of 0.1 A g$^{-1}$. 
Figure S21  Performance of AC electrode for Li-ion storage.
Figure S22  CV plots at 40 mV s\(^{-1}\) (A), GCD curves at 1 A g\(^{-1}\) (B), Ragone plots (C) and cycling behavior for 5000 cycles at 5 A g\(^{-1}\) (D) of 4.5 V-MnF\(_2\)//AC LICs (1:1) and 4.6 V-MnF\(_2\)//AC LICs (1:2).
Figure S23  The third cycle of CV curves under 0-5 V at 1 mV s\(^{-1}\): MnF\(_2\)//AC LICs (1:1) (A), MnF\(_2\)//AC LICs (1:2) (B).
Figure S24  CV plots of 4.5 V-MnF$_2$//AC LICs (1:1) at 10-160 mV s$^{-1}$ (A), GCD curves of 4.5 V-MnF$_2$//AC LICs (1:1) at 0.5-16 A g$^{-1}$ (B), CV plots of 4.6 V-MnF$_2$//AC LICs (1:2) at 10-160 mV s$^{-1}$ (C), GCD curves of 4.6 V-MnF$_2$//AC LICs (1:2) at 0.5-16 A g$^{-1}$ (D).
Figure S25  CV plots at 40 mV s\(^{-1}\) (A), GCD curves at 1 A g\(^{-1}\) (B), Ragone plots (C) and cycling behavior for 5000 cycles at 5 A g\(^{-1}\) (D) of 4 V-MnF\(_2\)/AC LICs (1:1), (1:2) and (1:3).
Figure S26  CV plots of 4 V-MnF₂-E//AC LICs (1:1) (A), 4 V-MnF₂-E//AC LICs (1:2) (C) and 4 V-MnF₂-E//AC LICs (1:3) (E) at 10-160 mV s⁻¹, GCD curves of 4 V-MnF₂-E//AC LICs (1:1) (B), 4 V-MnF₂-E//AC LICs (1:2) (D) and 4 V-MnF₂-E//AC LICs (1:3) (F) at 0.5-16 A g⁻¹.
**Figure S27** CV plots of 4 V-MnF₂//AC LICs (1:1) (A) and 4.3 V-MnF₂//AC LICs (1:1) (C) at 10-160 mV s⁻¹, GCD curves of 4 V-MnF₂//AC LICs (1:1) (B) and 4.3 V-MnF₂//AC LICs (1:1) (D) at 0.5-16 A g⁻¹.
Figure S28  CV plots of 4.3 V-MnF$_2$-E//AC LICs (1:2) (A), GCD curves of 4.3 V-MnF$_2$-E//AC LICs (1:2) (B) at 0.5-16 A g$^{-1}$. 
Figure S29  GCD curves of MnF$_2$ 8# (A) and MnF$_2$ 8#-E (B) at 0.1-1.6 A g$^{-1}$.
Figure S30  Rate performance and Coulombic efficiency of MnF$_2$ 8# (A) and MnF$_2$ 8#-E (B) electrodes at 0.1-1.6-0.1 A g$^{-1}$, Cycling stability and Coulombic efficiency of MnF$_2$ 8# (C) and MnF$_2$ 8#-E (D) electrodes at 0.3 A g$^{-1}$ for 500 cycles.
Figure S31  XRD patterns and TEM images of the MnF$_2$ 8# (A, C, E) and MnF$_2$ 8#-E (B, D, F) electrodes after the cycling for Na-ion storage.
Figure S32  The pseudocapacitive contributions (the shaded region) of the MnF$_2$ 8# electrode at 0.1-0.3 mV s$^{-1}$ (a-c) and the contribution ratios (d) for Na-ion storage.

Figure S33  The pseudocapacitive contributions (the shaded region) of the MnF$_2$ 8#-E electrode at 0.1-0.3 mV s$^{-1}$ (a-c) and the contribution ratios (d) for Na-ion storage.
Figure S34  Nyquist plots of MnF$_2$ 8# and MnF$_2$ 8#-E electrodes (the insets are the enlarged high frequency regions).
**Figure S35**  GCD curves of MnF$_2$ 8# (A) and MnF$_2$ 8#-E (B) electrodes at the precharged current density of 0.1 A g$^{-1}$. 
Figure S36  Performance of AC electrode for Na-ion storage.
Figure S37  CV plots at 40 mV s$^{-1}$ (A), GCD curves at 1 A g$^{-1}$ (B), Ragone plots (C) and cycling behavior for 5000 cycles at 3 A g$^{-1}$ (D) of 4.6 V-MnF$_2$/AC NICs (1:1) and 4.8 V-MnF$_2$/AC NICs (1:2).
Figure S38  The third cycle CV curves at 1 mV s\(^{-1}\) under 0-5 V: MnF\(_2\)/AC NiCs (1:1) (A), and MnF\(_2\)/AC NiCs (1:2) (B).
Figure S39  CV plots of 4.6 V-MnF$_2$/AC NICs (1:1) (A) and 4.8 V-MnF$_2$/AC NIC (1:2) (C) at 10-160 mV s$^{-1}$, GCD curves of 4.6 V-MnF$_2$/AC NIC (1:1) (B) and 4.8 V-MnF$_2$/AC NICs (1:2) (D) at 0.5-8 A g$^{-1}$. 
Figure S40  CV plots of 4 V-MnF$_2$/AC NICs (1:1) (A) and 4.3 V-MnF$_2$/AC NICs (1:1) (C) at 10-160 mV s$^{-1}$, GCD curves of 4 V-MnF$_2$/AC NICs (1:1) (B) and 4.3 V-MnF$_2$/AC NICs (1:1) (D) at 0.5-8 A g$^{-1}$. 
Figure S41  CV plots of 4 V-MnF$_2$-E//AC NICs (1:1) (A) and 4.3 V-MnF$_2$-E//AC NICs (1:1) (C) at 10-160 mV s$^{-1}$, GCD curves of 4 V-MnF$_2$-E//AC NICs (1:1) (B) and 4.3 V-MnF$_2$-E//AC NICs (1:1) (D) at 0.5-8 A g$^{-1}$. 
| Level | Solvent (mL)-A | Temperature (°C)-B | Time (h)-C |
|-------|----------------|-------------------|------------|
| 1     | NPA            | 180               | 6          |
| 2     | NBA            | 190               | 12         |
| 3     | EG             | 200               | 24         |

Note: NPA n-propyl alcohol; NBA n-butyl alcohol; EG ethylene glycol.

Table S1 Orthogonal experimental design.
| Samples | Mn(CH$_3$COO)$_2$•4H$_2$O (mmol) | HF (40%) (mL) | Solvent (mL) | Temperature (°C) | Time (h) |
|---------|--------------------------------|---------------|--------------|-----------------|---------|
| 1#      | 4                              | 7             | NPA 30       | 180             | 6       |
| 2#      | 4                              | 7             | NPA 30       | 190             | 12      |
| 3#      | 4                              | 7             | NPA 30       | 200             | 24      |
| 4#      | 4                              | 7             | NBA 30       | 180             | 12      |
| 5#      | 4                              | 7             | NBA 30       | 190             | 24      |
| 6#      | 4                              | 7             | NBA 30       | 200             | 6       |
| 7#      | 4                              | 7             | EG 30        | 180             | 24      |
| 8#      | 4                              | 7             | EG 30        | 190             | 6       |
| 9#      | 4                              | 7             | EG 30        | 200             | 12      |

**Table S2** Synthesis condition of MnF$_2$ 1#-9#.
## MnF$_2$

The optimal conditions selected are A3B2C1 or A3B2C3.

### Table S3 Orthogonal experimental analysis results of MnF$_2$

| Samples | Experimental factors | Specific capacity (mAh g$^{-1}$) | Rate retention (%) | Cycle retention (%) |
|---------|----------------------|----------------------------------|-------------------|--------------------|
| A       | B                    | C                               |                   |                    |
|         | (solvent)            | (temperature)                    | (time)            |                    |
| 1#      | 1 (NPA)              | 1 (180°C)                        | 1 (6h)            | 154                | 42                | 118               |
| 2#      | 1 (NPA)              | 2 (190°C)                        | 2 (12h)           | 163                | 42                | 153               |
| 3#      | 1 (NPA)              | 3 (200°C)                        | 3 (24h)           | 146                | 43                | 144               |
| 4#      | 2 (NBA)              | 1 (180°C)                        | 2 (12h)           | 151                | 49                | 129               |
| 5#      | 2 (NBA)              | 2 (190°C)                        | 3 (24h)           | 150                | 46                | 142               |
| 6#      | 2 (NBA)              | 3 (200°C)                        | 1 (6h)            | 149                | 47                | 145               |
| 7#      | 3 (EG)               | 1 (180°C)                        | 3 (24h)           | 143                | 51                | 147               |
| 8#      | 3 (EG)               | 2 (190°C)                        | 1 (6h)            | 162                | 54                | 141               |
| 9#      | 3 (EG)               | 3 (200°C)                        | 2 (12h)           | 144                | 51                | 145               |

Specific capacity: B>C>A  
Rate retention: A>C>B  
Cycle retention: B>C>A  

The optimal conditions: A3B2C3 or A3B2C1

Selected optimal conditions: A3B2C1
| Devices | Samples | Li//MnF$_2$ LIBs | Na//MnF$_2$ LIBs |
|---------|---------|------------------|------------------|
| MnF$_2$ 1# | 145 | 128 | 112 | 94 | 81 | 65 | 161 | 168 |
| MnF$_2$ 2# | 149 | 137 | 125 | 109 | 89 | 67 | 123 | 160 |
| MnF$_2$ 3# | 137 | 130 | 119 | 104 | 84 | 68 | 113 | 153 |
| MnF$_2$ 4# | 145 | 136 | 125 | 111 | 94 | 74 | 109 | 138 |
| MnF$_2$ 5# | 143 | 132 | 120 | 105 | 87 | 70 | 107 | 153 |
| MnF$_2$ 6# | 143 | 133 | 125 | 112 | 97 | 80 | 128 | 154 |
| MnF$_2$ 7# | 135 | 125 | 118 | 106 | 90 | 74 | 121 | 151 |
| MnF$_2$ 8# | 153 | 146 | 137 | 124 | 108 | 89 | 138 | 152 |
| MnF$_2$ 9# | 136 | 127 | 118 | 106 | 89 | 74 | 120 | 154 |
| MnF$_2$ 8#-E | 411 | 346 | 285 | 235 | 179 | 120 | 271 | 207 |
| MnF$_2$ 8# | 31 | 19 | 10 | 4 | 2 | - | 5.4 | 90 |
| MnF$_2$ 8#-E | 59 | 22 | 14 | 6 | 4 | - | 11 | 77 |

**Table S4** Summary of performance of MnF$_2$ 1#-9# and MnF$_2$ 8#-E electrodes.
| Anode materials for LIBs | Specific capacity | Rate behavior | Cycle life | Refs. |
|-------------------------|-------------------|---------------|------------|-------|
| MnF₂                    | 300 mA h g⁻¹      | 180 mA h g⁻¹  | 237 mA h g⁻¹ | 5000 / 10 C | Adv. Energy Mater., 2015, 5, 1401716 |
| CoF₂                    | 350 mA h g⁻¹      | #             | 15.5%      | Electrochim. Acta, 2015, 168, 225-233 |
| Mn₃O₄                   | 180 mA h g⁻¹      | #             | 15.9%      | ACS Appl. Mater. Interfaces, 2012, 4, 1636–1642 |
| NbO₂F                   | 250 mA h g⁻¹      | #             | 72%        | J. Power Sources, 2006, 162, 1312–1321 |
| Mn-O-F (MnF₂-E)         | 411 mA h g⁻¹      | 120 mA h g⁻¹  | 271 mA h g⁻¹ | 500 / 2 A g⁻¹ | This work |

Table S5 A comparison for Mn-O-F (MnF₂ 8#-E) anode with literature for LIBs.
| Systems (LIBs) | Model $R(QR)W(QR)$ | $R_s$ (Ω) | $Q_1$ (S·sec$^n$) | $n_1$ | $R_0$ (Ω) | $W$ (S·sec$^{0.5}$) | $Q_2$ (S·sec$^n$) | $n_2$ | $R_e$ (Ω) | $\chi^2$ |
|---------------|---------------------|-----------|--------------------|------|-----------|-------------------|--------------------|------|-----------|------|
| MnF$_2$ 1#     |                     | 3.419     | 4.772×10$^{-4}$   | 0.9674 | 56.95     | 0.03817           | 1.893×10$^{-5}$    | 0.8383 | 3.508×10$^5$ | 2.73×10$^{-3}$ |
| MnF$_2$ 2#     |                     | 3.713     | 4.931×10$^{-4}$   | 0.9614 | 59.62     | 0.2168            | 1.584×10$^{-5}$    | 0.8519 | 1.144×10$^5$ | 2.1×10$^{-3}$  |
| MnF$_2$ 3#     |                     | 3.372     | 1.508×10$^{-5}$   | 0.8458 | 59.79     | 0.02511           | 6.573×10$^{-4}$    | 0.9681 | 3.17×10$^6$  | 3.07×10$^{-3}$ |
| MnF$_2$ 4#     |                     | 3.549     | 1.423×10$^{-5}$   | 0.8667 | 62.33     | 0.02601           | 7.544×10$^{-4}$    | 0.9733 | 5.186×10$^5$ | 2.95×10$^{-3}$ |
| MnF$_2$ 5#     |                     | 3.917     | 8.254×10$^{-4}$   | 0.9672 | 68.34     | 0.02364           | 1.57×10$^{-5}$     | 0.8555 | 4.375×10$^5$ | 2.53×10$^{-3}$ |
| MnF$_2$ 6#     |                     | 3.935     | 1.614×10$^{-5}$   | 0.8575 | 63.11     | 0.02576           | 7.698×10$^{-4}$    | 0.9708 | 5.645×10$^5$ | 2.43×10$^{-3}$ |
| MnF$_2$ 7#     |                     | 3.34      | 1.395×10$^{-5}$   | 0.8741 | 44.46     | 0.05389           | 8.176×10$^{-4}$    | 0.9665 | 4.665×10$^5$ | 2.98×10$^{-3}$ |
| MnF$_2$ 8#     |                     | 3.171     | 1.435×10$^{-5}$   | 0.8711 | 46.13     | 0.01497           | 6.862×10$^{-4}$    | 0.9751 | 4.267×10$^5$ | 2.8×10$^{-3}$  |
| MnF$_2$ 9#     |                     | 3.126     | 5.98×10$^{-4}$    | 0.9724 | 43.09     | 0.02385           | 1.835×10$^{-5}$    | 0.8639 | 3.111×10$^5$ | 3.41×10$^{-3}$ |
| MnF$_2$ 8#-E   |                     | 3.411     | 2.26×10$^{-5}$    | 0.8418 | 37.33     | 0.0168            | 3.506×10$^{-3}$    | 0.8056 | 6427       | 3.61×10$^{-3}$ |

**Table S6**  EIS parameters of MnF$_2$ and MnF$_2$ 8#-E electrodes for Li-ion storage.
| Systems           | Voltage window | Energy density (Wh kg⁻¹) | Power density (kW kg⁻¹) | Cycling behavior |
|-------------------|----------------|--------------------------|-------------------------|------------------|
|                   |                | 0.5 A g⁻¹                | 4 A g⁻¹                 | 16 A g⁻¹         | 0.5 A g⁻¹     | 4 A g⁻¹     | 16 A g⁻¹     |                  |
| MnF₂//AC (1:1)    | 0-4.0 V        | 69.2                     | 46.7                    | 31.1             | 0.5           | 4.0         | 16.0          | 5 A g⁻¹ /1000/79.4% |
|                   | 0-4.3 V        | 82.9                     | 52.5                    | 38.2             | 0.54          | 4.3         | 17.2          | 5 A g⁻¹ /1000/63.5% |
|                   | 0-4.0 V        | 106.8                    | 71.1                    | 41.4             | 0.33          | 2.7         | 10.7          | 5 A g⁻¹ /1000/66.5% |
| MnF₂-E//AC (1:2)  | 0-4.3 V        | 132.2                    | 79.6                    | 44.6             | 0.36          | 2.9         | 11.5          | 5 A g⁻¹ /1000/63.5% |
|                   | 0-4.0 V        | 16.4                     | 8.3                     | 4.4              | 0.5           | 2.0         | 8.0           | 3 A g⁻¹ /200/62.5%  |
|                   | 0-4.3 V        | 37                       | 18.5                    | 7.2              | 0.54          | 2.1         | 8.6           | 3 A g⁻¹ /200/66.7%  |
|                   | 0-4.0 V        | 42.1                     | 28.4                    | 8.9              | 0.5           | 2.0         | 8.0           | 3 A g⁻¹ /200/63.1%  |
|                   | 0-4.3 V        | 55.9                     | 36.8                    | 19.2             | 0.54          | 1.9         | 7.7           | 3 A g⁻¹ /200/51.7%  |

Table S7  Summary of performance of MnF₂//AC and MnF₂-E//AC LICs and NICs.
| Systems            | Voltage window / V | Energy density / Wh kg\(^{-1}\) | Power density / kW kg\(^{-1}\) | Cycling behavior / retention%, repeated cycles, current density | Refs. |
|--------------------|--------------------|---------------------------------|--------------------------------|---------------------------------------------------------------|--------|
| TiSe\(_{0.8}S\_1.4\)//AC | 0.0-2.6            | 50-14                           | -                              | 69%/5000/1 A g\(^{-1}\)                                      | 1      |
| TiO\(_2\)-rGO//AC   | 1.0-4.5            | 42-8.9                          | 0.8-8.0                        | 80%/100/0.4 A g\(^{-1}\)                                    | 2      |
| CNT/V\(_2O_5\)//AC  | 1.8-4.0            | 25.5-6.9                        | 0.04-6.3                       | -                                                             | 3      |
| TiO\(_2\)-B//CNT    | 0.0-2.8            | 23-7                            | 0.14-2.8                       | 73%/1200/1.5 A g\(^{-1}\)                                    | 4      |
| TiO\(_2\) belt///graphene | 0.0-3.8       | 82-21                           | 0.57-19                        | 73%/600/1 A g\(^{-1}\)                                      | 5      |
| TiO\(_2\)@EEG//EEG  | 0.0-3.0            | 72-10                           | 0.303-2.0                      | 68%/1000/1.5 A g\(^{-1}\)                                    | 6      |
| MnF\(_2\) 8#//AC\((1:1)\) | 0-4.0             | 69.2-31.1                       | 0.5-16.0                       | 72.5%/5000/5 A g\(^{-1}\)                                    |        |
|                    | 0-4.3              | 82.9-38.2                       | 0.54-17.2                      | 63.5%/1000/5 A g\(^{-1}\)                                    | This work |
| MnF\(_2\) 8#-E//AC\((1:2)\) | 0-4.0             | 106.8-41.4                      | 0.33-10.7                      | 63.4%/3000/5 A g\(^{-1}\)                                    |        |
|                    | 0-4.3              | 132.2-44.6                      | 0.36-11.5                      | 60.8%/2000/5 A g\(^{-1}\)                                    |        |

Note: EEG graphene nanosheets; CNT carbon nanotube; rGO Reduced Graphene Oxide

**Table S8** Electrochemical performance comparison for some reported LICs.
| Systems (NIBs) | $R_s$ ($\Omega$) | $Q_1$ (S·sec) | $n_1$ | $R_{ct}$ ($\Omega$) | $W$ (S·sec$^{-1/2}$) | $Q_2$ (S·sec$^{1/2}$) | $n_2$ | $R_e$ ($\Omega$) | $\chi^2$ |
|---------------|-----------------|--------------|-------|-------------------|----------------|----------------|-------|----------------|--------|
| MnF$_2$ 8#    | 3.68            | 6.526×10$^{-4}$ | 0.9872 | 144.8             | 0.004796       | 1.366×10$^{-3}$ | 0.8916 | 2.154×10$^{-14}$ | 3.26×10$^{-4}$ |
| MnF$_2$ 8#-E  | 3.632           | 1.468×10$^{-5}$ | 0.8627 | 106.7             | 8.269×10$^{-7}$ | 1.775×10$^{-3}$ | 0.6392 | 4.173×10$^{-15}$ | 4.23×10$^{-5}$ |

**Table S9** EIS parameters of MnF$_2$ 8# and MnF$_2$ 8#-E electrodes for Na-ion storage.
| Systems                              | Voltage window / V | Energy density / Wh kg\(^{-1}\) | Power density / kW kg\(^{-1}\) | Cycling behavior / retention%, repeated cycles, current density | Refs. |
|-------------------------------------|--------------------|----------------------------------|-------------------------------|---------------------------------------------------------------|-------|
| NiCo\(_2\)O\(_4\)/AC               | 0-3.0              | 23.5-13.8                        | 0.036-0.308                   | 61.2%/2000/ 0.15 A g\(^{-1}\)                                | 7     |
| Na\(_{0.44}\)MnO\(_2\)             | 0-1.6              | 27.9-15                          | 0.012-0.24                    | -                                                             | 8     |
| /Na\(_{0.44}\)MnO\(_2\)            |                    |                                  |                               |                                                              |       |
| V\(_2\)O\(_5\)/CNT/AC              | 0-2.8              | 38-7.5                           | 0.14-5.0                      | -                                                             | 9     |
| Na-TNT/AC                           | 0-3.0              | 34-13                            | 0.15-0.89                     | 80%/1000/ 0.25 A g\(^{-1}\)                                  | 10    |
| MnF\(_2\) 8#/AC (1:1)               | 0-4.3              | 37-7.2                           | 0.54-8.6                      | 66.7%/100/ 3 A g\(^{-1}\)\(^\#\)                             |       |
|                                     |                    |                                  |                               | 66.7%/300/ 3 A g\(^{-1}\)\(^#\)                               |       |
|                                     |                    |                                  |                               | 58.4%/500/ 3 A g\(^{-1}\)\(^#\)                               |       |
|                                     |                    |                                  |                               | 58.4%/800/ 3 A g\(^{-1}\)\(^#\)                               |       |
|                                     |                    |                                  |                               | 88.8%/100/ 3 A g\(^{-1}\)\(^*\)                               |       |
|                                     |                    |                                  |                               | 88.8%/300/ 3 A g\(^{-1}\)\(^*\)                               | This  |
|                                     |                    |                                  |                               | 77.9%/500/ 3 A g\(^{-1}\)\(^*\)                               | work  |
|                                     |                    |                                  |                               | 77.9%/800/ 3 A g\(^{-1}\)\(^*\)                               |       |
| MnF\(_2\) 8#/E/AC (1:1)             | 0-4.0              | 42.1-8.9                         | 0.5-8.0                       | 68.4%/100/ 3 A g\(^{-1}\)\(^@\)                              |       |
|                                     |                    |                                  |                               | 63.1%/200/ 3 A g\(^{-1}\)\(^@\)                               |       |
|                                     |                    |                                  |                               | 52.7%/500/ 3 A g\(^{-1}\)\(^@\)                               |       |
|                                     |                    |                                  |                               | 52.7%/800/ 3 A g\(^{-1}\)\(^@\)                               |       |
|                                     |                    |                                  |                               | 86.7%/100/ 3 A g\(^{-1}\)\(^@\)                              |       |
|                                     |                    |                                  |                               | 80.0%/200/ 3 A g\(^{-1}\)\(^@\)                               |       |
|                                     |                    |                                  |                               | 67.2%/500/ 3 A g\(^{-1}\)\(^@\)                               |       |
|                                     |                    |                                  |                               | 67.2%/800/ 3 A g\(^{-1}\)\(^@\)                               |       |

Note: \# Based on the 1\(^{st}\) cycle; * Based on the 5\(^{th}\) cycle; @ Based on the 20\(^{th}\) cycle

Table S10  Electrochemical performance comparison for some reported NICs.
| Chemicals, agents and materials | Type or level | Company                      | Detailed characteristics or parameters |
|--------------------------------|---------------|------------------------------|-----------------------------------------|
| Mn(CH₃COO)₂•4H₂O               | AR            | SinoPharm                   | purity≥99.0%                            |
| HF                             | AR            | Zhanyun                     | purity≥40.0%                            |
| EG                             | AR            | SinoPharm                   | purity≥99.0%                            |
| NPA                            | AR            | SinoPharm                   | purity≥99.0%                            |
| NBA                            | AR            | SinoPharm                   | purity≥99.0%                            |
| NMP                            | AR            | SinoPharm                   | purity≥99.0%                            |
| NaBH₄                          | AR            | SinoPharm                   | purity≥96.0%                            |
| AB                             | Battery grade | /                            | /                                       |
| PVDF                           | Battery grade | /                            | /                                       |
| Li plate                       | Battery grade | China Energy                | 15.6*0.45 mm                            |
| Na plate                       | Battery grade | /                            | /                                       |
| Cu foil                        | 200*0.015     | GuangZhou                   | Total thickness: 15 μm; weight: 87 g m⁻² |
| Carbon coated-Al foil          | 222*0.015     | GuagZhou                    | Total thickness: 17 μm; Strength: 192 Mpa |
| Glass microfiber filters       | GF/D 2.7 μm; 1823-025 | Whatman                  | Diameter: 25 mm; Thickness: 675 μm; weight: 121 g m⁻² |
| AC                             | YEC 8b        | Fuzhou YiHuan               | D50: ~10 μm; Density: 0.4 g cm⁻³; SSA:2000~2500 m² g⁻¹ |
| Li-ion electrolytes            | LBC-305-01    | CAPCHEM                     | 1 M LiPF₆ /EC:EMC:DMC (1:1:1) /1% VC 0.85 M NaPF₆ /EC:DEC (1:1) / 5% FEC |
| Na-ion electrolytes            | /             | MJS                         | /                                       |
| Cell components                | CR-2032       | Shenzhen                    | /                                       |

Table S11  Chemicals, agents and materials.
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