Supporting Information

## Anion-Cation Synergistic Interactions for Low-Temperature and

**Fast-Charging Performance in Sodium Batteries** 

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## **Experimental Section**

**Preparation of electrolyte:** The following chemicals were purchased: sodium hexafluorophosphate (NaPF<sub>6</sub>, Adamas), lithium hexafluorophosphate (LiPF<sub>6</sub>, Adamas), Lithium bis (trifluoromethanesulfonyl) imide (LiTFSI, Adamas), Lithium difluorosulfonylimide (LiFSI, Adamas), Lithium difluorophosphate (LiDFP, Adamas), Lithium tetrafluoroborate (LiBF<sub>4</sub>, Adamas), diglyme (G2, Adamas), sodium tetrafluoroborate (NaBF<sub>4</sub>, Aladdin), hard carbon (HC, Kuraray). The 1M-BG2 electrolyte is prepared by dissolving 0.01 M NaBF4 into 10 mL of G2 solvent. The preparation process for the 1M-BG2-LP, 1M-BG2-LTF, 1M-BG-LF, 1M-BG2-LD and 1M-BG2-LBF electrolytes involves the addition of 1.5 mM of compounds LiPF<sub>6</sub>, LiTFSI, LiFSI, LiDFP and LiBF<sub>4</sub> to 10 mL of DEGDME solvent containing 0.01 M NaBF<sub>4</sub>, respectively.

## **Preparation of electrode:**

**Electrodes for Coin Cells:** The NFPP cathode was prepared with a mass ratio of 85% NFPP, 8% PVDF, and 7% Super-P carbon, achieving a loading of 3.8–4.0 mg·cm<sup>-2</sup>. The HC anode was fabricated with a mass ratio of 80% HC, 10% PVDF, and 10% Super-P carbon, with a loading of 1.0~1.2 mg·cm<sup>-2</sup>. All symmetric and hal cells were assembled using a PP/PE-based separator in the form of CR2016.

**Electrodes for Pouch Cells:** The NFPP cathode was composed of 93% NFPP, 4% PVDF and 3% Super-P carbon by weight, with an NFPP loading of approximately 13.6–14.5 mg·cm<sup>-2</sup>. The HC anode consisted of 95% HC, 1.5% CMC, 2.5% SBR, and 1% Super-P carbon. Prior to use, CMC and SBR binders were dispersed in water,

resulting in an HC loading of around 6 mg·cm<sup>-2</sup>. The N/P capacity ratio for the NFPP||HC pouch cells was 1.15. All cells were assembled in an Ar-filled glovebox (O<sub>2</sub> < 0.1 ppm, H<sub>2</sub>O < 0.1 ppm).

**Material characterizations:** Microscopic imaging was performed with scanning electron microscopy (SEM, HITACHI SU3800), transmission electron microscopy (TEM, Thermo Scientific Talos F200X G2), and atomic force microscopy (AFM, Oxford MFP-3D). Spectroscopic analysis was conducted with Raman spectroscopy (Renishaw inVia Qontor), Fourier-transform infrared spectroscopy (FTIR, SHIMADZU IRAffinity-1S), and nuclear magnetic resonance (NMR, Bruker AVANCE NEO 700 MHz). The surface chemistry of the cycled electrodes was examined using X-ray photoelectron spectroscopy (XPS, SHIMADZU Kratos AXIS UltraDLD) and time-of-flight secondary ion mass spectrometry (TOF-SIMS, ION TOF TOF SIMS 5-100).

**Electrochemical measurements:** Electrochemical impedance spectroscopy (EIS) was performed with an electrochemical workstation (Princeton VersaSTAT 4), over a frequency range of 10 mHz to 1 MHz. The C-rate was defined as 1C = 100 mA/g. The Na||Na symmetric cells were charged and discharged at a current density of 0.5~7 mA/cm<sup>2</sup>, with a capacity of 0.5~7 mAh/cm<sup>2</sup>.

Additional remarks: Electrochemical tests were performed at 25°C, unless otherwise stated.



Figure S1. (a) Distribution diagram of electrostatic potential for various solvation.



**Figure S2.** Na<sup>+</sup> radical distribution functions (RDFs) from MD simulation of (a) 1M-BG2 electrolyte and (b) 1M-BG2-LP electrolyte.



**Figure S3.** Snapshot and typical solvation structure obtained from MD simulation of (a) 1M-BG2 and (b) 1M-BG2-LP electrolyte at -20°C.



**Figure S4.** Solvation structure calculated by DFT: Changes in Free, CIP and AGGs Ratios in various electrolytes with temperature.



**Figure S5.** (a) The FT-IR spectra of C-O-C and (b) C-H stretching mode in various electrolytes at 25  $^{\circ}$ C and -20  $^{\circ}$ C.



**Figure S6.** Schematic illustration of the mechanism for mitigating battery polarization through the synergistic interaction of cations and anions. (a) The voltage plateau in Na||Na symmetric cells during the initial cycle  $(a_{1a}-a_{1e})$  and  $(a_{2a}-a_{2e})$  after 2000 hours/battery failure with various electrolytes, measured at 25 °C and a current density of 0.5 mA cm<sup>-2</sup> with a capacity of 0.5 mAh cm<sup>-2</sup>. (b) The voltage plateau in Na||Na symmetric cells during the initial cycle  $(b_{1a}-b_{1e})$  and  $(b_{2a}-b_{2e})$  after 2000 hours/battery failure with various electrolytes, measured at 25 °C and a current density of 1 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup>. (c) The voltage plateau in Na||Na symmetric cells during the initial cycle  $(c_{1a}-c_{1e})$  and  $(c_{2a}-c_{2e})$  after 2000 hours/battery failure with various electrolytes, measured at 25 °C and a current density of 1 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup>. (c) The voltage plateau in Na||Na symmetric cells during the initial cycle  $(c_{1a}-c_{1e})$  and  $(c_{2a}-c_{2e})$  after 2000 hours/battery failure with various electrolytes, measured at 25 °C and a current density of 1 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup>. (c) The voltage plateau in Na||Na symmetric cells during the initial cycle  $(c_{1a}-c_{1e})$  and  $(c_{2a}-c_{2e})$  after 2000 hours/battery failure with various electrolytes, measured at 25 °C and a current density of 3 mA cm<sup>-2</sup> with a capacity of 3 mAh cm<sup>-2</sup>.



**Figure S7.** The voltage plateau in Na||Na symmetric cells during the initial cycle after 2000 hours/battery failure in 1M-BG2-LBF electrolyte, measured at 25 °C and a current density of (a) and (b) 0.5 mA cm<sup>-2</sup> with a capacity of 0.5 mAh cm<sup>-2</sup>. (c) and (d) 1 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup>. (e) and (f) 3 mA cm<sup>-2</sup> with a capacity of 3 mAh cm<sup>-2</sup>.



**Figure S8.** SEM images of Na metal electrodes in various electrolytes after 100 cycles with a capacity of 3 mAh cm<sup>-2</sup> at 25 °C and a current density of 3 mA cm<sup>-2</sup>.



**Figure S9.** Cycling performance of Na||Na symmetrical cells with various electrolytes at 25 °C: (a) Cycling performance at a current density of 0.5 mA cm<sup>-2</sup> with a capacity of 0.5 mAh cm<sup>-2</sup> and (b) the corresponding voltage plateau after cycling for 5500h.



**Figure S10.** Cycling performance of Na||Na symmetrical cells with various electrolytes at 25 °C: (a) Cycling performance at a current density of 1 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup> and (b) the corresponding voltage plateau after cycling for 3000h.



**Figure S11.** Cycling performance of Na||Na symmetrical cells with various electrolytes at 25 °C: (a) Cycling performance at a current density of 3 mA cm<sup>-2</sup> with a capacity of 3 mAh cm<sup>-2</sup> and (b) the corresponding voltage plateau after cycling for 2000h.



**Figure S12.** (a) The voltage plateau at -20 °C under a current density of 0.5 mA cm<sup>-2</sup> with a capacity of 0.5 mAh cm<sup>-2</sup> after cycling for 5000h; (b) The voltage plateau at -20 °C under a current density of 1 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup> after cycling for 2156h; (c) The voltage plateau at -20 °C under a current density of 2 mAh cm<sup>-2</sup> after cycling for 100h.



Figure S13. The overpotential of various electrolytes at at -20 °C and 25 °C.



**Figure S14.** (a) Cycling performance of Na||Na symmetrical cells in 1M-BG2-LP electrolyte at 25 °C at a current density of  $0.5 \sim 7 \text{ mA cm}^{-2}$  with a capacity of  $0.5 \sim 7 \text{ mAh} \text{ cm}^{-2}$ 



**Figure S15.** (a) Nyquist plots of the Na||Na symmetric cells before and after cycling for 100 h in various electrolytes (the inset is the equivalent circuit used for fitting the Nyquist plots, where  $R_{SEI}$  and  $R_{ct}$  are respectively SEI resistance and charge-transfer resistance) and (b) the corresponding resistance ( $R_{SEI}$  and  $R_{ct}$ ) of fitting.



**Figure S16.** (a) Nyquist plots of the Na||Na symmetric cells in 1M-BG2-LP electrolyte during cycling. (b) The  $R_{SEI}$  and  $R_{ct}$  of fitting of the Na||Na symmetric cells in 1M-BG2-LP electrolyte during cycling.



Figure S17. The  $R_{SEI}$  and  $R_{ct}$  of fitting of the Na||Na symmetric cells in 1M-BG2-LP electrolyte at different temperatures.



**Figure S18.** Nyquist plots of the Na||Na symmetric cells in 1M-BG2 electrolyte during cycling.



**Figure S19.** a) Changes in XPS spectra of C1s, F1s, and P2p on the Na metal electrode after 100 cycles (symmetric Na||Na cells) in 1M-BG2-LP electrolyte at 25 °C, with Argon ion-beam sputtering time. b) Contents of Na, F, B, C, and P elements in the SEI on the Na metal electrode after 100 cycles (symmetric Na||Na cells) in 1M-BG2-LP electrolyte at 25 °C.



**Figure S20.** Electrochemical performance of HC||Na half cells: a) Nyquist plots of the HC||Na cells after 10 cycles in various electrolytes. Voltage profiles of Galvanostatic charge and discharge in b) 1M-BG2-LP electrolyte and c) 1M-BG2 electrolyte at 25 °C and -20 °C.



**Figure S21.** Electrochemical performance of HC||Na half cells: (a) Long-term cycling performance at 25 °C and 1C (HC||Na). (b) Rate capability at 25 °C and (c) the corresponding charge-discharge curves.



Figure S22. Long-term cycling performance at -20 °C and 1C (HC||Na).



**Figure S23.** Cycling performance of NFPP||HC pouch cells: (a) Long-term cycling performance at 25 °C and 1C. (b) HRTEM characterization of the SEI on the HC electrode cycled in 1M-BG2-LP electrolyte at 25 °C.



**Figure S24.** Cycling performance of NFPP||HC pouch cells: (a) Long-term cycling performance at -20 °C and 0.5C. (b) HRTEM characterization of the SEI on the HC electrode cycled in 1M-BG2-LP electrolyte at -20 °C. (c) The pouch cells of 0.5Ah.



Figure S25. (a) Young's modulus of tangents and (b) height distribution of tangents.