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Competitive Anion Coordination Modulates Anode Interfacial Chemistry for Wide-Temperature Sodium Batteries

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ABSTRACT

Sodium-ion batteries (SIBs) offer a promising, cost-effective alternative for large-scale energy storage due to the abundance of sodium. However, their practical deployment is challenged by sluggish interfacial kinetics and unstable interphase formation, which severely limit performance across wide temperature ranges. Here, we demonstrate that competitive coordination between strongly (OTF[−]) and weakly (PF₆[−]) coordinating anions can be harnessed to fundamentally modulate the anode interphase and solvation kinetics in hard carbon systems. Through integrated molecular dynamics simulations, spectroscopic analysis, and density functional theory, we reveal how PF₆[−] attenuates the excessive Na⁺–OTF[−] binding, thereby optimizing the solvation sheath for accelerated desolvation and promoting the formation of a uniform, fluorine-rich solid–electrolyte interphase with enhanced ionic transport and mechanical integrity. This tailored interface enables exceptional performance from −30°C to 60°C, including a capacity of 78.4 mAh g^{−1} at 5 A g^{−1} (room temperature), 77% capacity retention after 2600 cycles at −30°C, and stable high-rate operation at 60°C. Full cells and pouch cells assembled with hard carbon (HC) and commercial Na₄Fe₃(PO₄)₂(P₂O₇) (NFPP) were successfully charged and discharged at −20°C. This work unfolds competitive anion coordination as a fundamental principle governing interfacial chemistry and solvation dynamics, providing a mechanistic foundation for the rational design of wide-temperature sodium batteries.

1 | Introduction

The ongoing electrification of transport and the expansion of renewable energy grids are intensifying the need for energy storage technologies that remain effective under diverse and demanding operational environments [1–3]. Presently, the market is heavily reliant on lithium-ion batteries, a technology

supported by extensive manufacturing infrastructure and proven capability across a spectrum of applications [4]. However, the continued dependence on this platform is confronted by serious economic and technical obstacles. These include the finite nature of global lithium reserves, inflationary pressures on key raw material costs, and a well-documented decline in electrochemical performance at suboptimal temperatures [5, 6].

Mingxing Zhang and Tengfei Jiang are co-first authors and have contributed equally to this work.

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Such limitations highlight a pressing need to engineer next-generation storage solutions that can overcome these specific hurdles to enable wider deployment [7].

In response to these limitations, significant research focus has shifted to post-lithium battery technologies, motivated by their prospects for greater resource abundance, lower cost, and improved operational safety [8]. Sodium-ion batteries (SIBs) have emerged as a particularly compelling alternative among systems based on calcium, magnesium, or zinc. SIBs operate on an energy storage mechanism analogous to LIBs but benefit from the widespread availability of sodium, offering a cost-effective profile and notably better capacity retention in cold climates [9]. Nevertheless, the pursuit of higher energy density and robust power delivery under extreme conditions remains a critical challenge for SIBs [10]. Their performance is intrinsically limited by the larger ionic radius of Na^+ (1.02 vs. 0.76 Å for Li^+) and the higher resistance of the anode-side solid–electrolyte interphase (SEI) [11]. Within the SIB architecture, hard carbon (HC) stands out as a leading anode candidate, prized for its conductive and structurally stable properties for Na^+ hosting. However, its commercial implementation is hampered by a low initial coulombic efficiency (ICE, typically $\leq 85\%$), ongoing interfacial side reactions, and an SEI that becomes increasingly brittle at low temperatures [12]. Consequently, research has pursued multiple avenues to enhance HC performance, including expanding interlayer spacing to facilitate Na^+ intercalation and diffusion, optimizing porous structures, and introducing heteroatom doping or functional groups to elevate ICE and interfacial stability [13]. For example, Hou and colleagues demonstrated a cellulose-grafting technique for biomass pyrolysis, producing a hard carbon material with a graphitic nanodomain structure that enabled a full cell with $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{O}_2\text{F}$ to retain 86% capacity after 1000 cycles at 0.5 A g $^{-1}$ [14]. In another study, Song et al. developed curved carbon layers incorporating CoN_4 moieties from ZIF-67, achieving remarkably low-temperature performance with capacities of 288.7 and 270.0 mAh g $^{-1}$ at -20°C and -40°C , respectively [15].

Although these material-level modifications improve ionic and electronic conductivity, they frequently fail to concurrently achieve high capacity and high efficiency under rigorous high-rate and low-temperature operation [16]. Moreover, their commercial scalability is often limited by complex, energy-intensive synthesis processes and associated environmental concerns. Beyond intrinsic electrode kinetics, the rate capability of HC is profoundly influenced by interfacial charge transfer, a process encompassing ion desolvation at the SEI, interfacial ion transport, and ion–solvent diffusion [17]. This understanding has redirected attention toward interface engineering, particularly through electrolyte design. Drawing from lithium-ion battery research, strategies involving functional additives and weakly solvating electrolytes are being adapted to SIBs to refine interfacial properties [18]. The nature of the SEI is dictated by the electrolyte composition. In conventional polar solvents, Na^+ solvation leads to an organic-rich SEI containing species such as sodium alkyl carbonates. Although this layer is flexible and ionically conductive, its mechanical weakness causes perpetual fracture, triggering continuous electrolyte decomposition, gas generation, and rapid capacity decay [19]. Common carbonate

solvents such as propylene carbonate form a hybrid SEI with inorganic Na_2CO_3 , but their high flammability introduces significant safety hazards [20]. Thus, the development of safe, wide-temperature electrolytes that foster a stable SEI, inhibit its dissolution, and streamline interfacial ion transport is paramount [21]. Ether-based electrolytes have shown considerable promise in this regard, offering superior interfacial compatibility with HC anodes due to their low melting points and distinctive solvation behavior [22]. Empirical studies confirm that dual-solvent systems and specific additives in ether-based electrolytes can markedly enhance the ICE of HC at low temperatures while improving bulk-phase and interfacial compatibility [23]. A key advantage of ethers over esters lies in their tendency to facilitate competitive coordination from both solvent molecules and anions via ion–dipole and ion–ion interactions, respectively. This coordination environment lowers the Gibbs free energy for Na^+ desolvation and promotes the formation of a robust, electrolyte-derived SEI that underpins exceptional cycling performance [24]. Illustrating this, Tang et al. developed a weakly solvating electrolyte with tetrahydrofuran (THF) and NaPF_6 , enabling a commercial HC anode to achieve high-rate capability (5 A g $^{-1}$) and stable operation at -20°C [12]. In a parallel approach, Zheng et al. incorporated a double-layer modulator (TMSOTf) into an ether electrolyte, which promotes in situ radical generation and disrupts solvent ordering to drive interfacial reconstruction [25]. This strategy yielded exceptional stability, with commercial HC enduring 2400 cycles even at -40°C , highlighting a viable path for high-performance SIBs under extreme conditions. Drawing upon accumulated electrochemical knowledge of sodium salts, Wang and coworkers constructed a candidate molecular library and, through machine learning combined with multiobjective optimization, identified an organoboron-centered sodium salt, $\text{NaB}(\text{C}_2\text{H}_5)_4$, which exhibits a suitable oxidation decomposition potential and a high theoretical sodium compensation capacity [26]. Based on this design, a dual-salt electrolyte comprising 1 M NaPF_6 dissolved in a diethylene glycol dimethyl ether (G2)/1,3-dioxolane (DOL)/FEC mixture with $\text{NaB}(\text{C}_2\text{H}_5)_4$ was formulated, enabling stable cycling of $\text{HC}||\text{NaFe}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ pouch cells at -60°C . The initial coulombic efficiency increased from 64.8% for the blank electrolyte to 83.7%, and the cell retained 90.2% of its initial capacity after 200 cycles at -60°C . Although dual-salt and diluted electrolyte strategies have been extensively reported for sodium-ion batteries, it is still necessary to critically elucidate the fundamental mechanisms by which anion coordination governs temperature-dependent solvation behavior and interfacial chemistry.

Herein, we systematically elucidate the mechanistic linkage between anion-regulated solvation, desolvation kinetics, and SEI formation chemistry, demonstrating the effectiveness of competitive anion coordination in enabling wide-temperature sodium storage in hard carbon anodes. A screening of common solvents and sodium salts using density functional theory (DFT) calculations identified G2 as an optimal solvent, selected for its suitable highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy levels, low melting point, and high dielectric constant. The designed electrolyte employs a dual-salt system in G2, combining strongly coordinating NaOTf (high ion-pair binding energy) with weakly coordinating NaPF_6 . This configuration significantly enhances

Na⁺ diffusion compared to conventional single-salt electrolytes. Comprehensive characterization, including Raman spectroscopy, nuclear magnetic resonance (NMR), and solvation structure simulations, confirms that the balanced anion coordination optimizes the proportion of free to bound solvent molecules, thereby accelerating charge transfer in both the bulk electrolyte and at the electrode interface. Consequently, Na-HC cells utilizing this electrolyte demonstrate stable operation across an extensive temperature range, from −30°C to 60°C. These insights provide a deeper understanding of low-temperature interfacial chemistry and establish a foundational principle for the rational design of next-generation electrolytes, with significant implications for developing high-performance batteries for extreme environments.

2 | Experimental

2.1 | Electrolyte and Electrode Preparation

The battery-grade diethylene glycol dimethyl ether (DEGDME, G2), sodium trifluoromethanesulfonate (NaOTf), and sodium hexafluorophosphate (NaPF₆) (all with purity ≥ 99.8%) were purchased from Suzhou Dodo Chemical Technology Co. Ltd. The sodium salts and solvent were mixed at precise stoichiometric ratios and magnetically stirred for 24 h to ensure complete dissolution, yielding the “1 M NaPF₆” and “1 M NaOTf” electrolytes, respectively. Specifically, to prepare the hybrid electrolyte (denoted as “HE”), NaOTf and NaPF₆ were mixed at a 4:1 M ratio. All electrolytes were prepared at a constant total salt concentration of 1 M.

The HC electrodes were prepared by mixing hard carbon powder (Kuraray Type 2, purchased from Canrd Technology Co. Ltd.), sodium carboxymethyl cellulose (CMC, MAC500LC, KJ MTI), and styrene-butadiene rubber emulsion (SBR, ZEON, Japan) in a weight ratio of 90:5:5. Note that CMC was predissolved to form a 2-wt% aqueous solution, whereas SBR was used as a 40-wt% aqueous dispersion. The mixture was ball-milled for 6 h to form a homogeneous slurry, which was then coated onto a copper foil. The coated electrode was predried at 80°C for 6 h, cut into disks with a diameter of 12 mm, and subsequently pressed. The disks were then stored in vials and further vacuum-dried at 120°C for 12 h. The active material loading was approximately 2–2.5 mg cm^{−2}. The Na₄Fe₃(PO₄)₂P₂O₇ electrodes were fabricated by mixing Super P and poly(vinylidene fluoride) (PVDF) in a weight ratio of 8:1:1, grinding the mixture for 40–50 min until homogeneous, adding a few drops of NMP solution to form a paste, coating it evenly on aluminum foil (12 mm), and drying it at 80°C for 6 h to obtain cathodes with a mass loading of ~2.15 mg cm^{−2}.

2.2 | Electrochemical Measurements

All cells were assembled in a glovebox (Mikrouna) with water and oxygen levels maintained below 0.01 ppm, using sodium metal disks (12 mm diameter) as the counter electrodes. Electrochemical testing was conducted using coin cells (CR2032) on an electrochemical workstation (CHI 660f, Shanghai Chenhua, China), a NEWARE battery test system (CT-4008Tn, China), and a wide-temperature test system (AT MARS, AH-80D). Tafel plots were measured using Na||Na symmetric cells in the voltage range of −0.1 to 0.1 V at a scan rate of 2 mV s^{−1}. The nucleation

overpotential was characterized by cyclic voltammetry (CV) using Na||Al@C (carbon-coated aluminum foil) cells from −0.1 to 0.5 V at 2 mV s^{−1}. Coulombic efficiency was evaluated in Na||Al@C cells within a voltage window of 0.01–0.5 V. For hard carbon (HC) cells, cyclic tests were performed under different current densities with a testing potential range of 0.01–1 V. The galvanostatic intermittent titration technique (GITT) was applied to Na||HC cells. Prior to GITT measurement, the cells were subjected to 10 charge–discharge cycles at 0.01 A g^{−1} to stabilize their electrochemical performance. The GITT measurement consisted of a 30-min pulse current followed by a 1-h rest interval. Cyclic voltammetry of the Na||HC cells was performed at scan rates of 0.2, 0.4, 0.6, 0.8, and 1.0 mV s^{−1}. For low- and high-temperature testing, cells were first placed at the target temperature for more than 1 h to ensure thermal equilibration. Electrolyte resistance was obtained from the intercept of Nyquist plots from electrochemical impedance spectroscopy (EIS), with an applied frequency range of 0.01–105 Hz. Prior to long-term cycling, all Na||HC cells underwent one initial charge–discharge cycle at 0.05 A g^{−1} to activate the HC material.

2.3 | Electrolyte and Electrode Characterizations

Raman spectroscopy of the electrolyte was performed using a confocal microscope (WiTec alpha 300R) equipped with a 532-nm excitation laser. The electrolyte was sealed in an NMR tube to prevent exposure to air and moisture. After 50 charge–discharge cycles, the composition of the SEI on the hard carbon anode was characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). NMR spectroscopy was carried out using a Bruker AVANCE 400 spectrometer (400 MHz) with deuterated dimethyl sulfoxide (DMSO-d₆) as the solvent to investigate the solvation structure and intermolecular interactions in the electrolyte. The surface morphology of the electrodes after cycling was examined by scanning electron microscopy (SEM, Hitachi SU8020). X-ray diffraction (XRD) measurements were carried out on a Rigaku MiniFlex 600C instrument manufactured in Japan. The surface composition and depth stratification information of cycled HC electrodes were obtained via TOF-SIMS (TOF-SIMS IONTOF M6 instrument, IONTOF GmbH) measurements.

2.4 | Theoretical Calculations

All quantum chemistry calculations were conducted using the Gaussian 16 package [27]. The geometries of Na⁺–solvent (anion) complexes were optimized using the B3LYP functional with Grimme's D3BJ (Becke–Johnson damping) dispersion correction and the 6-311++G(d,p) basis set [28–31]. Frequency analyses were performed to confirm that all optimized structures correspond to potential minima, with no imaginary frequency modes. Free energies were calculated using the M06-2X functional with Grimme's D3 dispersion correction and the def2-TZVP basis set, combined with the solvation model based on charge density (SMD) for implicit solvation [32, 33]. G2 was used as the solvent for all Na⁺–complex calculations. The binding energies of Na⁺ in the electrolytes were determined using the following formula:

$$E_{\text{binding}} = E_{\text{complex}} - E_{\text{solvent/anion}} - E_{\text{Na}^+}, \quad (1)$$

where E_{complex} , E_{Na^+} , and $E_{\text{solvent/anion}}$ represent the total energy of the Na^+ cluster, the energy of the isolated Na^+ , and the energy of the solvent/anion, respectively.

Molecular dynamics (MD) simulations were performed using the GROMACS package with the OPLS-AA force field [34, 35]. The molecular parameters were generated using the LigParGen web server, except for the restrained electrostatic potential (RESP) atomic partial charges, which were derived from electrostatic potential (ESP) charges using the Multiwfn program [36, 37]. Three electrolyte systems were constructed: (1) NaPF_6 - NaOTf -G2 (8 NaPF_6 and 32 NaOTf molecules with 282 G2 molecules), (2) NaPF_6 -G2 (40 NaPF_6 molecules with 282 G2 molecules), and (3) NaOTf -G2 (40 NaOTf molecules with 282 G2 molecules). Each system was initially energy-minimized using the steepest descent and conjugate gradient (CG) algorithms. Equilibration was first performed under the NVT ensemble at 298 K for 5 ns using the Nosé-Hoover thermostat, followed by 5 ns under the NPT ensemble at 298 K and 1 bar controlled by the Parrinello-Rahman barostat. The system was then heated to 400 K over 5 ns and maintained at 400 K for another 5 ns, followed by annealing back to 298 K over 5 ns. Subsequently, all systems were equilibrated under the NPT ensemble at 298 K for 10 ns. A final 10-ns production run was conducted under the NVT ensemble using the Nosé-Hoover thermostat.

3 | Results and Discussion

The ion desolvation process is a critical rate-limiting step in battery operation, significantly influencing performance at both room and low temperatures [38]. To advance the commercialization of SIBs, electrolyte solvents must satisfy several key criteria: (1) a wide liquid-phase temperature range, characterized by a low melting point and a high boiling point for all-temperature operation; (2) a high dielectric constant to facilitate salt dissociation and increase free-ion concentration; (3) electrochemical stability, reflected by a low HOMO energy level (resistant to oxidation) and a high LUMO energy level (resistant to reduction); and (4) commercial viability, including abundant availability and low cost [39, 40]. Guided by these principles, various common solvents were evaluated from categories including linear ethers, cyclic ethers, furans, and alcohols. The assessment, detailed in Figure 1A and Supporting Information S1: Figures S1-S4 and Table S1, compared melting points, boiling points, dielectric constants, and DFT-calculated HOMO/LUMO energy levels. G2 emerged as the optimal candidate, exhibiting a combination of low HOMO and LUMO energy levels, a low melting point, a high boiling point, a moderate dielectric constant, and acceptable cost. Although G2 is slightly more expensive than conventional carbonate solvents (e.g., EC/DMC), carbonate solvents can, under certain conditions, cointercalate with Na^+ into the carbon layers of HC anodes, leading to structural degradation. In contrast, ether-based solvents, owing to their smaller molecular dimensions and weaker interactions with Na^+ , tend to promote the intercalation of desolvated Na^+ ions, thereby preserving the structural integrity of the anode [41]. Furthermore, G2 demonstrates superior environmental friendliness compared to many other ether-based solvents and has been widely documented for its high compatibility with sodium metal anodes [42, 43]. Based on

these comprehensive evaluations, G2 was selected as the solvent for this study.

The desolvation kinetics of Na^+ are determined by the binding energy of Na^+ with both solvent molecules and anions in the solvation sheath [44]. Although 1 M NaPF_6 in G2 electrolyte functions well with sodium metal anodes at room temperature, its performance declines at elevated and subambient temperatures [45]. This can be attributed to the weak binding between Na^+ and PF_6^- , which favors the formation of solvent-separated ion pairs (SSIPs) with a high energy barrier for desolvation [46]. Therefore, the effectiveness of electrolyte anions depends critically on operating temperature. To identify an anion that could modify this solvation structure, theoretical calculations on several common sodium salts were performed, that is, NaPF_6 , NaFSI , NaClO_4 , NaTFSI , and NaOTf . As shown in Figure 1B, NaOTf exhibits the strongest binding energy between Na^+ and OTf^- , favoring the formation of a contact ion pair (CIP) or even an aggregated ion pair (AGG) [47]. In such configurations, OTf^- anions tend to coordinate within the solvation shell, reducing the number of solvent molecules, consequently enhancing the mobility of Na^+ [48]. However, excessively strong coordination can overly suppress salt dissociation, limiting the concentration of free Na^+ ions and thus compromising ionic conductivity [49]. To balance these effects, a hybrid electrolyte was formulated by dissolving NaPF_6 and NaOTf dual salts in G2 and denoted as "HE." This dual-salt design strategically leverages the weak coordination of PF_6^- to maintain a high concentration of free Na^+ , whereas the strong coordination of OTf^- introduces a stable population of AGG/CIP (Figure 1C). It is expected that this tailored solvation environment will synergistically improve ionic conductivity and desolvation kinetics, enabling robust electrolyte performance across a wide temperature range.

Raman spectroscopy was conducted on three electrolytes, that is, 1 M NaPF_6 , 1 M NaOTf , and the dual-salt electrolyte (HE) (detailed compositions are provided in the Supporting Information), to elucidate the Na^+ solvation structure (Figure 1D-F). The Raman peak of free G2 was deconvoluted into three Gaussian components located at 802.3, 824.2, and 848.5 cm^{-1} , corresponding to CH_2 rocking modes and C-O-C stretching modes, labeled as F1, F2, and F3, respectively [50-52]. The vibrational peaks of solvated G2 were observed at 839.4, 861.1, and 870.3 cm^{-1} , designated as S1, S2, and S3, respectively. In the conventional 1 M NaPF_6 system, the proportion of free G2 (41.37%) is lower than that of solvated G2 (58.63%), consistent with the weak Na^+ - PF_6^- binding energy and a solvation sheath dominated by SSIPs. In contrast, the 1 M NaOTf system exhibits a higher proportion of free G2 (50.3%) compared to solvated G2 (49.7%), reflecting the strong attraction between Na^+ and OTf^- and a greater tendency to form CIPs and AGGs. This highlights the role of strongly coordinated OTf^- in facilitating desolvation kinetics. The HE electrolyte exhibits an intermediate distribution between these two single-salt systems. NMR spectroscopy was further employed to probe the Na^+ solvation environment at the atomic scale. Compared to the 1 M NaPF_6 electrolyte, the ^{19}F NMR spectrum of the HE electrolyte exhibits a downfield shift (Figure 1G), indicating deshielding of the fluorine nuclei and a reduction in electron density around PF_6^- , which suggests a weakened interaction between PF_6^- and Na^+ [53]. Furthermore,

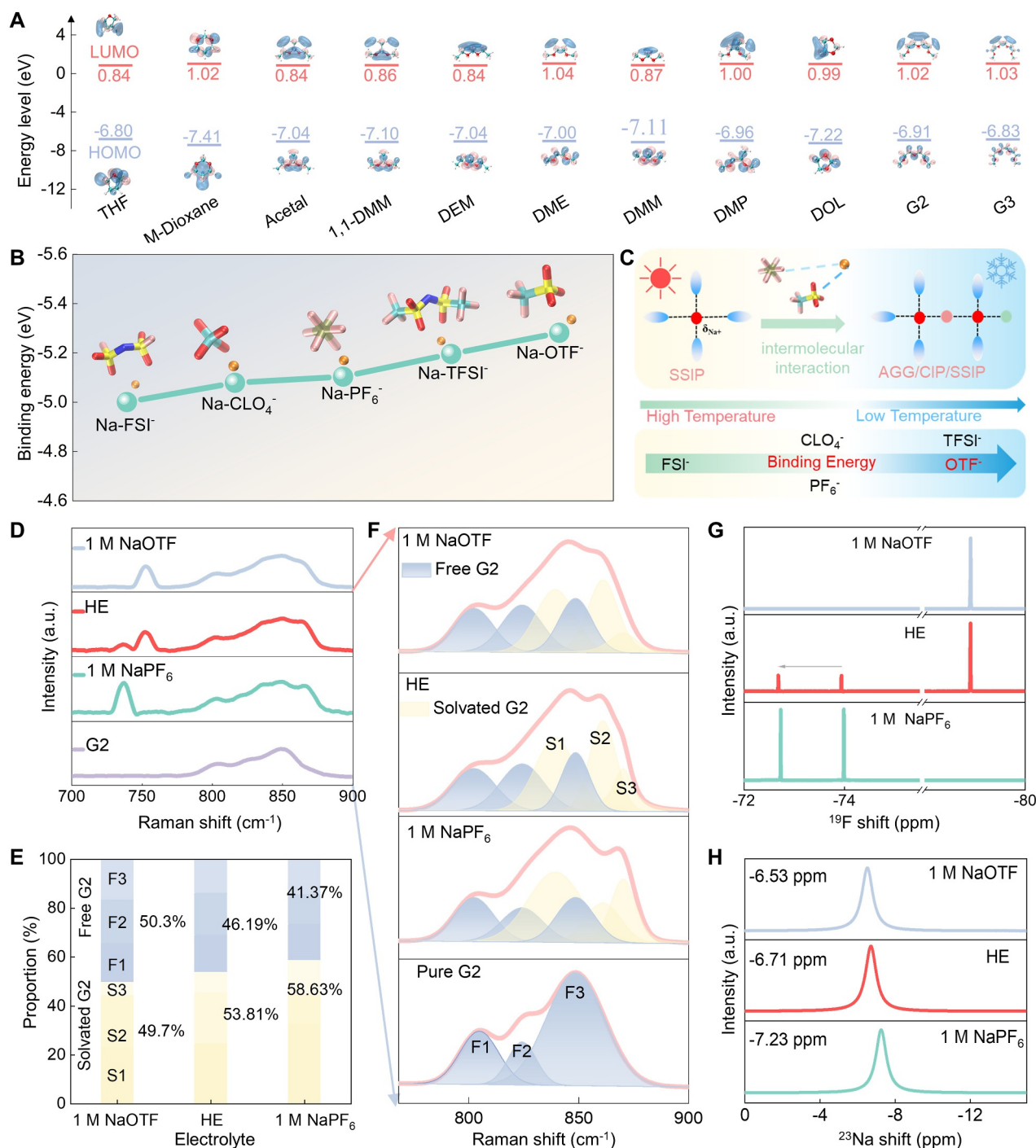


FIGURE 1 | Rational electrolyte design and characterization. (A) Screening of solvent frontier orbital energy levels (HOMO/LUMO), THF: tetrahydrofuran, M-Dioxane: 1,3-diethylene dioxide, 1,1-DMM: 1,1-dimethoxyethane, DEM: diethoxy methane, DME: 1,2-dimethoxyethane, DMM: dimethoxymethane, DMP: 1,2-dimethoxypropane, DOL: 1,3-dioxolane, G2: diethylene glycol dimethyl ether, G3: triethylene glycol dimethyl ether. (B) DFT-calculated Na⁺-anion binding energies for anion selection. (C) Proposed mechanism for solvation structure regulation through balanced anion coordination. (D, F) Raman spectral analysis and (E) the derived ratio of free to coordinated solvent molecules. (G, H) ¹⁹F and ²³Na NMR spectra elucidating the local chemical environments in different electrolytes.

the ²³Na NMR signals of the NaOTF and HE electrolytes display an upfield shift from -6.71 ppm (1 M NaPF₆) to -6.53 ppm (Figure 1H), consistent with the deshielding of Na⁺ due to a modified coordination environment with increased anion participation. Collectively, these results confirm that the introduction of OTF⁻ weakens the interaction between Na⁺ and G2 solvent molecules, thereby increasing the population of free G2

and optimizing the solvation structure for enhanced charge transfer [54].

Molecular dynamics (MD) simulations were performed to elucidate the microscopic solvation structures of the electrolytes. Analyses included the radial distribution function (RDF) with coordination numbers, snapshots of solvation structures,

and the probable composition of the primary solvation shell at 298 K. In the 1 M NaPF₆ system, a substantial population of free anions persists in the bulk electrolyte, whereas cations exhibit strong coordination with G2 molecules (Figure 2A). In contrast, both the 1 M NaOTf and HE electrolytes show a significant reduction in free anions (Figure 2B,C), which instead aggregate into cluster-like structures (Figure 2D). To quantify the local environment of Na⁺, RDFs for Na⁺-O (G2), Na⁺-F(PF₆⁻), and Na⁺-O(OTf⁻) were calculated (Figure 2E and Supporting Information S1: Figures S5 and S6). In both 1 M NaPF₆ and 1 M NaOTf electrolytes, distinct peaks near 2.4 Å confirm that G2, PF₆⁻, and OTf⁻ participate in the first solvation shell of Na⁺. Notably, no characteristic peaks corresponding to PF₆⁻ were detected in the HE electrolyte, indicating that PF₆⁻ modulates

the solvation structure while remaining largely excluded from the primary Na⁺ solvation sheath. Coordination number analysis reveals distinct solvation behaviors in the three electrolyte systems (Figure 2F). In the conventional 1 M NaPF₆ system, Na⁺ is coordinated predominantly by G2 molecules, with minimal PF₆⁻ involvement, resulting in a low abundance of free G2. Conversely, the strong Na⁺-OTf⁻ binding in the 1 M NaOTf electrolyte displaces some G2 from the solvation shell, increasing the population of free G2, consistent with Raman data. In the HE electrolyte, Na⁺-G2 coordination increases, whereas OTf⁻ coordination decreases compared to the pure NaOTf electrolyte. The lack of PF₆⁻ coordination confirms that its weak interaction modulates the overly strong Na⁺-OTf⁻ binding, thereby restructuring the Na⁺ solvation environment

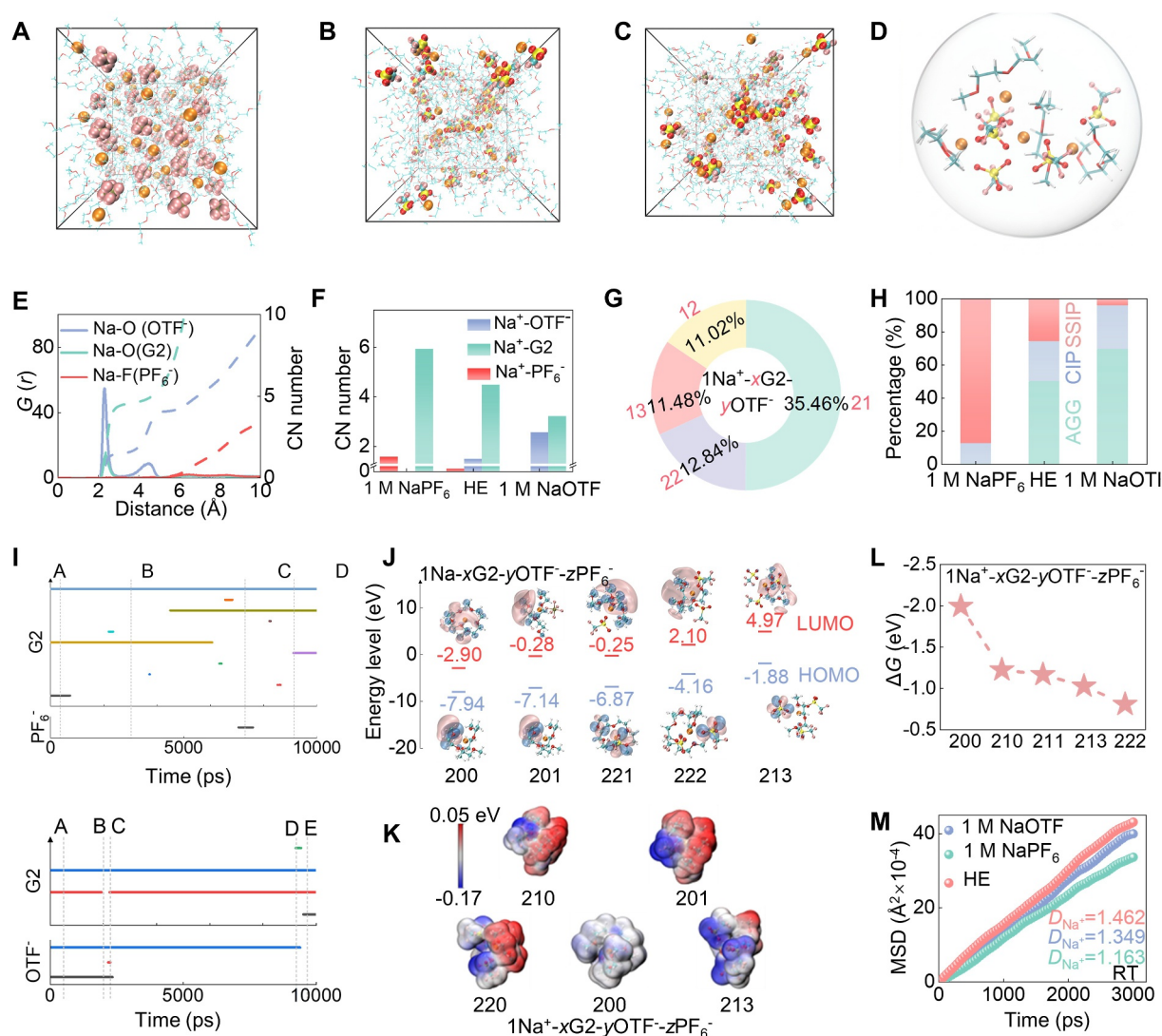


FIGURE 2 | Theoretical characterization of electrolyte solvation structures at 298 K. MD simulation snapshots of (A) 1 M NaPF₆, (B) 1 M NaOTf, and (C) HE electrolytes. (D) Representative anion-cluster structure observed in the HE electrolyte. (E) Radial distribution functions (RDFs) of Na⁺ with O(G2), F(PF₆⁻), and O(OTf⁻) in the HE electrolyte. (F) Coordination numbers of Na⁺ with anions and solvent molecules across the three electrolytes. (G) Distribution of dominant primary solvation-shell compositions in the HE electrolyte. (H) Relative percentages of solvent-separated ion pair (SSIP), contact ion pair (CIP), and aggregate ion pair (AGG). (I) Evolution of the Na⁺ solvation environment obtained from MD trajectories. (J) HOMO/LUMO energy levels of four representative solvation configurations. (K) Electrostatic potential map of the Na⁺(O-G2)₁(O-OTf⁻)₃ cluster. (L) Calculated interfacial desolvation energies for the same configurations. (M) Diffusion coefficients of Na⁺ derived from mean-square-displacement analysis. The atoms are color-coded as follows: C, cyan; P, slate green; H, white; O, red; S, pale yellow; F, pink; N, blue; Na, orange-yellow.

and altering the ratio of free to bound G2. Analysis of the primary solvation-shell distribution (Figure 2G and Supporting Information S1: Figure S7 and Tables S2–S4) identified Na^+ (O-G2)₃ as the most probable configuration in 1 M NaPF₆. For both the 1 M NaOTF and HE electrolytes, the dominant average environment is Na^+ (O-G2)₂(OTF[−])₁. This configuration is more prevalent in the HE electrolyte, demonstrating that NaPF₆ enhances G2 coordination, yielding an intermediate Na^+ –G2 coordination number between the two single-salt systems. Finally, the proportions of SSIP, CIP, and AGG in the three electrolytes were quantified based on MD simulations, as shown in Figure 2H. The 1 M NaPF₆ electrolyte is dominated by SSIPs (~87.43%) with minimal AGGs (0.11%). In stark contrast, the 1 M NaOTF electrolyte exhibits a high AGG content (69.5%) and very few SSIPs (4.17%). The HE electrolyte achieves a balanced structure with an intermediate AGG population (50.15%) and a more even distribution of CIP (24.09%) and SSIP (25.76%) (structural schematics in Supporting Information S1: Figure S8). In summary, the strongly coordinating OTF[−] predominantly facilitates the formation of CIPs and AGGs. In contrast, weakly coordinating PF₆[−] favors a moderate population of SSIPs. The resulting balanced ion-pair equilibrium prevents excessive aggregation-induced viscosity rise and mitigates the high desolvation energy barrier characteristic of SSIP-dominated solvation structures, thereby facilitating efficient Na^+ transport and interfacial kinetics.

To elucidate the mechanism by which balanced anion coordination modulates electrolyte properties, MD simulations were employed to probe Na^+ solvation dynamics, including anion and solvent residence times over 10,000 ps (Figure 2I and Supporting Information S1: Figures S9–S11). In the 1 M NaPF₆ electrolyte, PF₆[−] exhibits a short residence time, consistent with its minimal role in coordination. Conversely, OTF[−] in the 1 M NaOTF electrolyte shows a markedly longer residence time, reflecting its strong interaction with Na^+ . In the HE electrolyte, the residence time of PF₆[−] is even shorter, confirming its negligible coordination, whereas the solvation structure remains dominated by G2 and OTF[−], aligning with the established weak coordination of PF₆[−] and the strong coordinating ability of OTF[−].

DFT calculations were performed to assess the influence of OTF[−] and PF₆[−] on redox stability and (de)solvation behavior. The frontier orbital energy levels of dominant solvation configurations in the HE electrolyte were computed. The most prevalent configuration, Na^+ (O-G2)₂(O-OTF[−])₁, exhibits a relatively low LUMO and a high HOMO. As OTF[−] occupies more coordination sites, such as Na^+ (O-G2)₂(O-OTF[−])₂ and Na^+ (O-G2)₁(O-OTF[−])₃, the HOMO energy rises substantially, indicating reduced oxidation stability. The proportion of such high-HOMO configurations is greater in the 1 M NaOTF electrolyte, explaining its inferior oxidation resistance compared to the HE electrolyte. The electrostatic potential map (Figure 2K) reveals that negative charge is predominantly localized on the anions, with OTF[−] being especially negative. This distribution accounts for the highest LUMO energy observed for the Na^+ (O-G2)₁(O-OTF[−])₃ cluster (Figure 2J). As shown in Figure 2L and Supporting Information S1: Figure S12, the interfacial desolvation energy of Na^+ decreases progressively with greater

OTF[−] participation in the solvation shell. Furthermore, the Na^+ diffusion coefficients at 298 K, derived from mean-square-displacement analysis over 3000 ps (Figure 2M), follow the order: HE ($1.462 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$) > 1 M NaOTF ($1.349 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$) > 1 M NaPF₆ ($1.163 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$). Ionic conductivity measurements (Supporting Information S1: Figure S13) highlight the superior performance of the HE electrolyte at both room temperature and low temperature. Notably, its ionic conductivity reaches 0.871 ms cm^{-1} at -30°C , nearly twice that of the 1 M NaPF₆ electrolyte (0.427 ms cm^{-1}), which can be attributed to the accelerated Na^+ transport kinetics within the HE electrolyte. These results demonstrate that excessively strong or weak anion coordination hinders Na^+ diffusion via distinct mechanisms, whereas a balanced combination of strongly and weakly coordinating anions in G2-based electrolytes effectively facilitates Na^+ desolvation and enhances ion transport.

A significant drawback of NaOTF-based electrolytes is their propensity to form an unstable and mechanically weak solid-electrolyte interphase (SEI) on sodium metal, which typically results in low CE, irregular deposition morphology, and dendritic growth [55]. To examine how the inclusion of NaPF₆ modifies the solvation environment and influences sodium deposition behavior, compatibility tests were performed using Na||Na and Na||Al@C (carbon-coated aluminum foil) cells. At a constant current density of 0.5 mA cm^{-2} and a fixed capacity of 1 mAh cm^{-2} , the electrolyte with 1 M NaOTF exhibited rather unstable stripping/plating behaviors with fluctuating CEs (Figure 3A), resulting in cell failure due to short-circuiting within 50 cycles. Conversely, the Na||Al@C cell employing the HE electrolyte achieved a CE of 99.9% within a few cycles and maintained a high average CE of ~99.9% over nearly 550 cycles (Figure 3B), demonstrating exceptional reversibility and long-term stability.

Cyclic voltammetry (CV) measurements at 2 mV s^{-1} revealed a higher nucleation overpotential for the HE electrolyte in Na||Al@C cells compared to the 1 M NaOTF system (Supporting Information S1: Figure S14), indicating a tendency toward smoother and more compact sodium deposition that suppresses dendrite growth. Repeated plating/stripping cycles in Na||Na symmetric cells at 0.5 mA cm^{-2} and 0.5 mAh cm^{-2} further demonstrated the stability of the HE electrolyte, with cells operating reliably for over 1400 h while maintaining a low overpotential (Figure 3C,D). Moreover, the cells can also be stably cycled over 1100 h at a low current density of 0.25 mA cm^{-2} and maintain steady cycling for 120 h even at a high current density of 2 mA cm^{-2} and a high areal capacity of 2 mAh cm^{-2} (Supporting Information S1: Figure S15). Additionally, the HE electrolyte exhibited a higher exchange current density for sodium plating/stripping (Supporting Information S1: Figure S16), consistent with its elevated Na^+ diffusion coefficient. These results collectively affirm that the incorporation of NaPF₆ facilitates interfacial kinetics, underscoring the superior reversibility of Na plating/stripping achieved through PF₆[−]-mediated solvation structure modulation in strongly coordinated electrolytes. To determine the optimal ratio, a systematic investigation was conducted on a series of molar ratios between NaOTF and NaPF₆ while maintaining a total salt concentration of 1 M. The electrolyte formulations

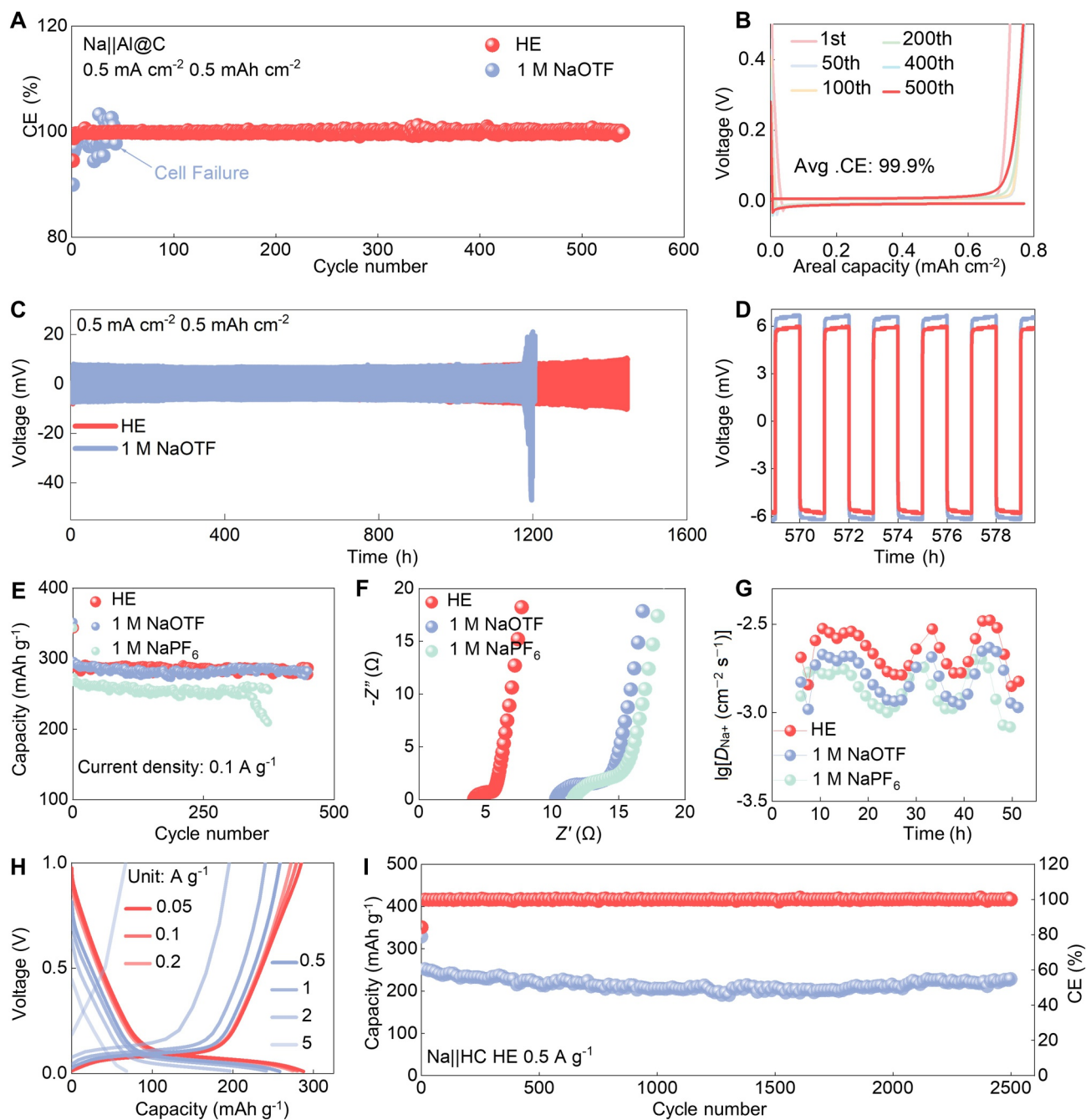


FIGURE 3 | Compatibility with sodium metal and hard carbon anodes at room temperature. (A, B) Coulombic efficiency and corresponding voltage profiles of Na||Al@C cells in 1 M NaOTF and HE electrolytes at 0.5 mA cm⁻² and 0.5 mAh cm⁻². (C, D) Galvanostatic cycling of Na||Na cells at 0.5 mA cm⁻² and 0.5 mAh cm⁻². (E) Cycle performance of Na||HC cells at 0.1 A g⁻¹ with different electrolytes. (F, G) EIS spectra and GITT profiles of Na||HC cells in different electrolytes. (H) Initial galvanostatic charge-discharge curves of Na||HC cells in HE electrolyte at different current densities. (I) Long-term cycling stability of Na||HC cell in HE electrolyte at 0.5 A g⁻¹.

were evaluated through Na||Na symmetric cell cycling tests at a current density of 0.5 mA cm⁻² with a fixed capacity of 0.5 mAh cm⁻². The selection criteria were based on two key electrochemical indicators: the magnitude of overpotential and long-term cycling stability. As shown in the Supporting Information (Supporting Information S1: Figure S17), the electrolyte with a NaOTF:NaPF₆ molar ratio of 2:8 exhibited the lowest overpotential and the most stable voltage profile over extended cycles. An excessively high proportion of NaOTF led to enhanced

polarization and unstable stripping behavior, attributed to overly strong Na⁺-OTF⁻ coordination and insufficient free Na⁺. Conversely, NaPF₆-dominated ratios resulted in sluggish plating kinetics and poor low-temperature performance, consistent with its weakly coordinating nature.

The electrochemical performance of the 1 M NaOTF, 1 M NaPF₆, and HE electrolytes was evaluated using commercial hard carbon (HC, Kuraray Type 2) anodes (detailed information

in the Supporting Information). As shown in Figure 3E and Supporting Information S1: Figure S18, cycling tests at 0.1 A g^{-1} demonstrate that the HE electrolyte surpasses both single-salt electrolytes in both cycling stability and ICE. The 1 M NaPF_6 electrolyte exhibited the lowest ICE and fastest capacity decay, which can be attributed to the weak $\text{Na}^+ - \text{PF}_6^-$ binding energy, resulting in slow Na^+ diffusion kinetics. In this context, interfacial charge-transfer resistance, Na^+ diffusion coefficient (D_{Na^+}), and polarization behaviors were probed using EIS, distribution of relaxation time (DRT) analysis, galvanostatic intermittent titration technique (GITT), and CV at varied scanning rates. The HE electrolyte consistently showed lower interfacial resistance, a higher average D_{Na^+} , and reduced polarization (Figure 3F,G and Supporting Information S1: Figures S19 and S20), confirming its efficacy in accelerating Na^+ transport. To further decode the time-domain kinetic information embedded in the EIS data, in situ EIS coupled with DRT analysis was performed (Supporting Information S1: Figure S21). Specifically, relaxation peaks at $\tau_1 \approx 10^{-1} - 1 \text{ s}$ correspond to charge-transfer resistance (R_{ct})-related processes, whereas peaks located at $\tau_2 \approx 1 - 10 \text{ s}$ reflect the diffusion resistance of Na^+ [56]. Across the three electrolytes, the HE system exhibits a markedly weaker peak intensity in the τ_1 region compared to the two single-salt counterparts. Although the HE electrolyte shows a relatively high main peak amplitude at τ_2 , parasitic polarization peaks at low frequencies are significantly suppressed, indicating mitigated interfacial diffusion resistance. Rate-capability evaluation further highlights the advantage of the HE design (Figure 3H and Supporting Information S1: Figures S22 and S23). Although the HE and 1 M NaOTf electrolytes deliver similar capacities at low rates (0.05 , 0.1 , and 0.2 A g^{-1}), the HE system displays markedly superior kinetics at high rates, retaining 205 mAh g^{-1} at 2 A g^{-1} and 78.4 mAh g^{-1} even at 5 A g^{-1} . In contrast, the 1 M NaOTf electrolyte suffers from severe capacity deterioration with increasing current density. Interestingly, although the 1 M NaPF_6 system underperforms at low rates, it surpasses the NaOTf -based electrolyte at high rates, underscoring the complementary roles of strongly and weakly coordinating anions. Figure 3I exhibits the long-term cycling stability of the cell, achieving a capacity retention as high as 82.03% after 2500 cycles at a current density of 0.5 A g^{-1} , with minimal polarization increase throughout cycling. Furthermore, the cell exhibits considerable stability across various high rates, including 0.2 , 2 , and 0.5 A g^{-1} (Supporting Information S1: Figure S24). Collectively, these results demonstrate that balancing strongly and weakly coordinating anions effectively modulates the electrolyte solvation structure, leading to enhanced ICE, cycling stability, and rate capability for hard carbon anodes in sodium-ion batteries.

To gain deeper insight into the influence of PF_6^- addition on the structural evolution of HC electrodes and the associated solid-electrolyte interphase (SEI) formation mechanism, the morphological changes of HC electrodes were examined using SEM after 50 charge-discharge cycles at 0.2 A g^{-1} in 1 M NaOTf and HE electrolytes (Figure 4A-D). In the 1 M NaOTf electrolyte, decomposition products on the HC electrode primarily exhibit a sheet-like morphology (Figure 4A,B). In contrast, the surface deposits observed in the HE electrolyte appear as fine, spiked features (Figure 4C,D), suggesting a

distinct mode of SEI formation. Notably, no significant cracking is observed, indicating that the addition of NaPF_6 does not cause structural damage to the HC electrode. The composition and spatial distribution characteristics of the SEI provide crucial insights into the interfacial behaviors regulated by the balanced anion coordination. XPS depth profiling was performed on the cycled HC electrodes (Figure 4E-H). In the $\text{C } 1\text{s}$ spectrum obtained from the 1 M NaOTf electrolyte (Figure 4E), the peak observed at 283.3 eV can be assigned to Na_xC (Supporting Information S1: Table S5), corresponding to characteristic graphite intercalation compounds [57, 58]. This indicates that a fraction of Na^+ ions intercalate into the hard carbon structure before a stable SEI forms. This irreversibly trapped “dead Na” promotes dendritic growth, which breaches the SEI and triggers continuous electrolyte decomposition and gas evolution [59]. In contrast, no characteristic Na_xC peak is observed for the HE electrolyte (Figure 4F). Furthermore, this electrolyte exhibits stronger signals of NaF and P-F species (decomposition products of PF_6^- anions), suggesting that non-coordinating PF_6^- anions diffuse to the HC anode surface and decompose effectively, thereby enriching the interphase with fluorine. As the sputtering time increases, the oxygen concentration declines, whereas the fluorine and sodium contents remain nearly constant, indicating a compositionally uniform SEI in the HE electrolyte. Moreover, the higher atomic fraction of F in the HE electrolyte (Supporting Information S1: Figure S25) compared to that in 1 M NaOTf ($1\% - 2\%$) further confirms that the balanced coordination of OTf^- (strong) and PF_6^- (weak) suppresses dendritic growth and builds a stable, fluorine-rich interface, which, in turn, facilitates efficient Na^+ transfer. Though PF_6^- minimally participates in the primary Na^+ solvation sheath, its indirect regulation of the solvation equilibrium attenuates excessive $\text{Na}^+ - \text{OTf}^-$ interactions, facilitating a uniform, fluorine-rich SEI that homogenizes interfacial Na^+ flux and mitigates dendrite formation. Furthermore, time-of-flight secondary ion mass spectrometry (TOF-SIMS) was employed to quantitatively analyze the depth distribution profiles of various SEI fragments on the HC anode cycled in the HE electrolyte (Figure 4G,H and Supporting Information S1: Figure S26). The results reveal that PF_6^- undergoes controlled interfacial decomposition during cycling, continuously generating inorganic SEI species including NaF and phosphorus-oxygen-containing compounds ($\text{P-O}_x\text{F}_y$). These compact inorganic constituents enhance the mechanical robustness of the passivation layer, effectively suppressing electrolyte decomposition and mitigating dendrite nucleation and propagation.

Under low-temperature conditions, the solvation structure of the 1 M NaPF_6 electrolyte is dominated by SSIPs (Supporting Information S1: Figure S27). This is because the dielectric constant of the solvent typically increases slightly at low temperatures, and the enhanced solvation capability under such conditions makes Na^+ more readily surrounded by solvent molecules. When Na^+ is encapsulated by a greater number of G2 molecules, its positive charge becomes effectively shielded, thereby weakening the coulombic attraction with the negatively charged PF_6^- . This leads to the expulsion of anions from the primary solvation sheath and a consequent decrease in the coordination number, which, in turn, increases the interfacial impedance and causes kinetic hysteresis. Because of the

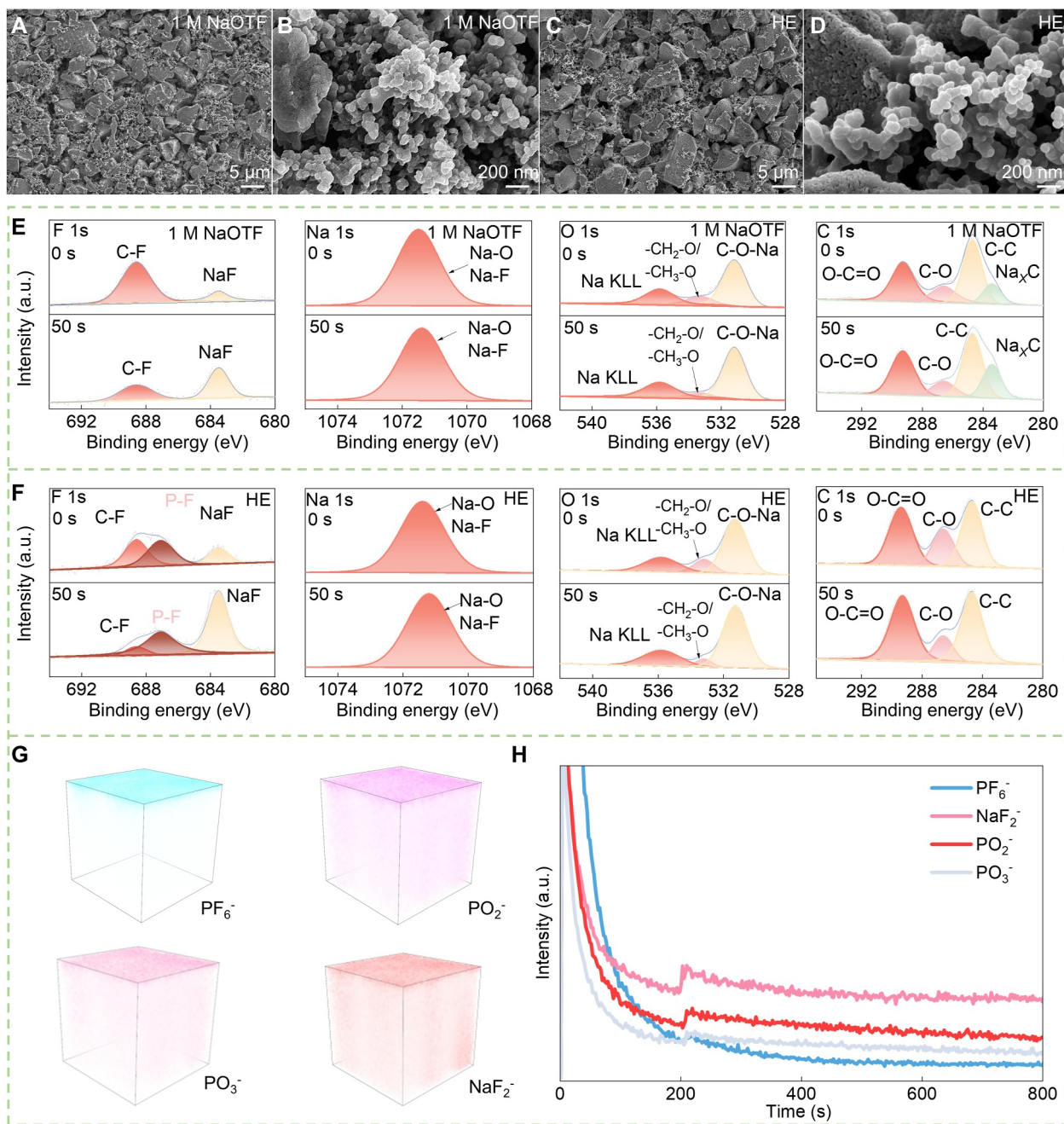


FIGURE 4 | Analysis of SEI composition and morphology derived from 1 M NaOTF and HE electrolytes. SEM images of HC electrodes from Na||HC cells after cycling for 50 cycles in (A, B) 1 M NaOTF and (C, D) HE electrolyte. XPS spectra (F 1s, Na 1s, O 1s, and C 1s) of HC anodes from Na||HC cells after cycling for 50 cycles in (E) 1 M NaOTF and (F) HE electrolyte. (G) 3D spatial distribution of PF_6^- , PO_2^- , PO_3^- , and NaF_2^- on the HC anode cycled with HE electrolyte detected by TOF-SIMS. (H) Depth profiles of the HC anode with HE electrolyte after cycling.

characteristics of solvent-ion interactions, such an electrolyte exhibits relatively low Na^+ ion conductivity, which may limit its applicability under extreme conditions [60]. Therefore, it is necessary to engineer the solvation structure to counterbalance the weak coordination ability of PF_6^- and thereby enhance Na^+ transport at low temperatures. MD simulations were further conducted at 243 K to reveal a contrasting thermal response in Na^+ solvation structures between the two electrolyte systems (Figure 5A–E and Supporting Information S1: Figure S28). In the HE electrolyte, cooling from 298 K to 243 K decreases the G2 coordination number from 4.49 to 4.375 while increasing OTF[−]

coordination from 1.49 to 1.775, shifting the equilibrium toward more CIPs and AGGs. This structural evolution weakens Na^+ –solvent interactions and enhances desolvation kinetics under low-temperature conditions. Conversely, the 1 M NaOTF electrolyte exhibits the opposite trend upon cooling: The G2 coordination number increases from 3.21 to 3.676, whereas OTF[−] coordination declines from 2.57 to 2.237, indicating strengthened Na^+ –solvent interaction and an increase in SSIP that impedes desolvation. These contrasting behaviors arise from distinct solvation thermodynamics. In the 1 M NaOTF system, the elevated dielectric constant and reduced thermal

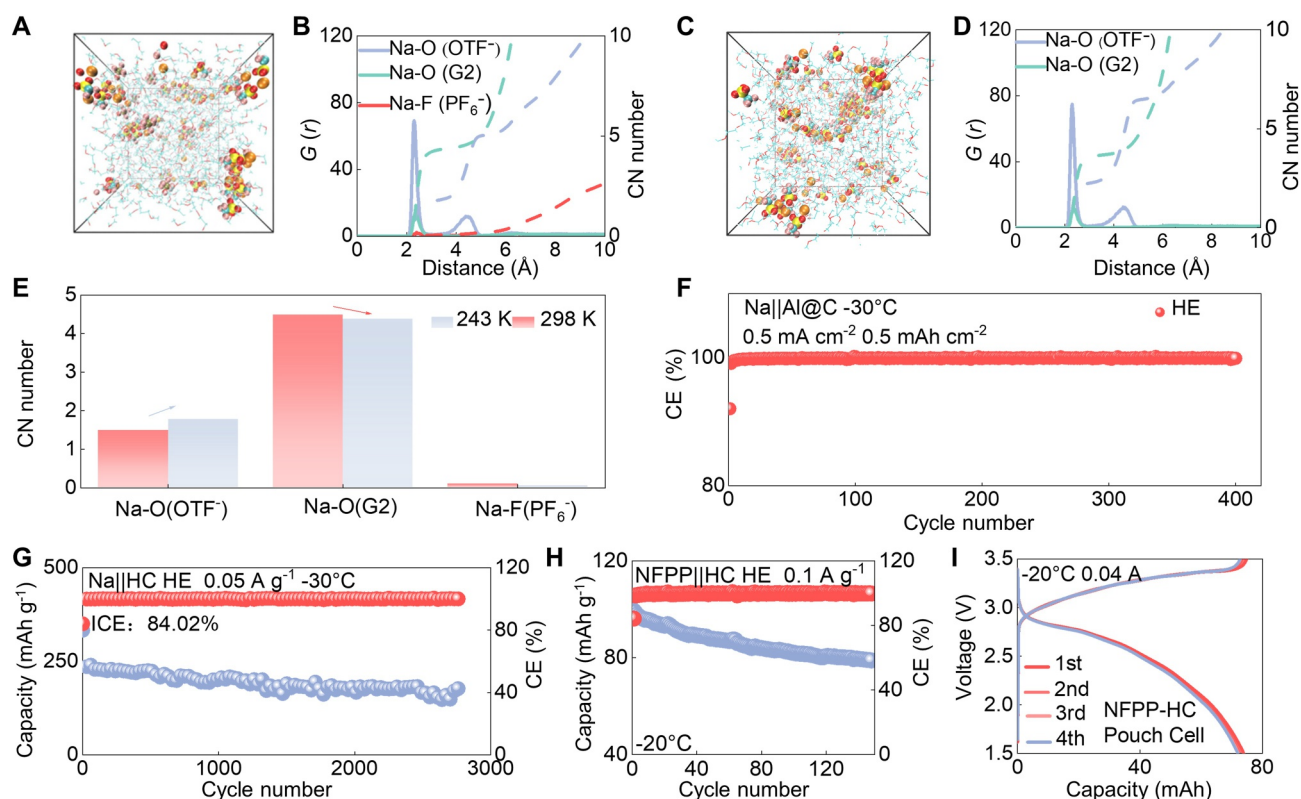


FIGURE 5 | Molecular dynamics and electrochemical analysis of low-temperature performance. Snapshots of solvation structures and corresponding RDFs for Na-O (G2), Na-F (PF₆⁻), and Na-O (OTF⁻) pairs at 243 K in (A, B) HE electrolyte and (C, D) 1 M NaOTF. (E) Temperature dependence of Na⁺ coordination numbers in the HE electrolyte from 298 K to 243 K. (F) Cycling stability of Na||Al@C cells at 0.5 mA cm⁻². (G) Electrochemical performance of Na||HC cell at -30°C. (H) Electrochemical performance of NFPP||HC cell at -20°C at 0.1 A g⁻¹. (I) Electrochemical performance of NFPP||HC pouch cell at -20°C at 0.04 A.

motion of G2 at low temperatures enhance its binding with Na⁺, allowing G2 to outcompete OTF⁻ and shift the equilibrium toward SSIP. In the HE system, non-coordinating PF₆⁻ generates a stronger electrostatic field at low temperatures, favoring Na⁺-OTF⁻ association to preserve charge neutrality. This promotes the formation of CIP and AGG, accelerating desolvation [61]. Thus, PF₆⁻ not only tempers the strong Na⁺-OTF⁻ coordination but also fundamentally reshapes the electrostatic equilibrium, thereby mitigating the sluggish desolvation kinetics typically observed at low temperatures [49]. Supporting Information S1: Figure S29 presents the polarization curves of Na||Na symmetric cells at -30°C. The HE electrolyte exhibits a transference number (T_{Na^+}) of 0.3, higher than that of the 1 M NaOTF electrolyte (0.25). This enhancement can be attributed to the PF₆⁻ anions weakening the intermolecular interactions between Na⁺ and G2 solvent molecules, thereby balancing the overly strong Na⁺-OTF⁻ coulombic interactions and facilitating Na⁺ transport. The reversibility of sodium plating/stripping at -30°C was evaluated using Na||Al@C cells (Figure 5F). At 0.5 mA cm⁻² and 0.5 mAh cm⁻², the cell with the HE electrolyte reached 99.9% CE within just a few cycles and maintained high stability over 400 cycles. Under the same conditions, Na||Na symmetric cells operated stably for nearly 1100 h at -30°C (Supporting Information S1: Figure S30), demonstrating exceptional sodium reversibility under cryogenic conditions. EIS on symmetric HC cells (Supporting Information S1: Figure S31) was used to compare interfacial Na⁺ transport. The activation

energy for Na⁺ desolvation was subsequently estimated from the EIS data using the Arrhenius law over 243–323 K [62]:

$$k = A \exp\left(\frac{-E_a}{RT}\right), \quad (2)$$

where k , A , E_a , R , and T represent the rate constant, pre-exponential constant, activation energy, standard gas constant, and absolute temperature, respectively. The introduction of NaPF₆ reduced the desolvation activation energy to 11.52 kJ mol⁻¹, confirming the superior low-temperature kinetics of the HE electrolyte.

To assess the practical viability of the balanced anion coordination strategy, the performance of Na||HC cells was systematically evaluated in the HE from -30°C to 60°C. As shown in Figure 5G, the Na||HC cell delivered a reversible capacity of 235 mAh g⁻¹ at -30°C, retaining 77% of its capacity after nearly 2600 cycles. At 60°C, it maintained a specific capacity of 166 mAh g⁻¹ even under an ultrahigh current rate of 5 A g⁻¹. Furthermore, the cell demonstrated stable operation at 60°C for 400 cycles at 1 A g⁻¹ with an ICE exceeding 85% and a retention rate of 75.22% (Supporting Information S1: Figure S32), highlighting its robust wide-temperature performance. Furthermore, to validate the practical viability of the as-designed HE electrolyte, the Na-ion full cell was assembled by pairing the commercial Na₄Fe₃(PO₄)₂(P₂O₇) (NFPP) cathode with the HC anode, and its cycling performance

was evaluated at -20°C . As shown in Figure 5H and Supporting Information S1: Figure S33, the Na-ion full cell delivers a reversible capacity of 99 mAh g^{-1} and exhibits stable cycling for nearly 140 cycles with a capacity retention of approximately 80%. The assembled pouch cell (Figure 5I) was successfully charged and discharged at -20°C , confirming its potential for commercial application. XRD and SEM characterizations were performed on NFPP electrodes before and after cycling to analyze the failure behavior and fully demonstrate the practical application potential of this electrolyte system, as shown in Supporting Information S1: Figures S34 and S35. At low temperatures, lattice distortion occurs in the NFPP cathode with impurity phase generation, which damages the SEI film on the anode. Accumulated decomposition byproducts and widespread surface cracks collectively shorten the cycling life of pouch cells. To further verify the effect of the HE electrolyte's uniform regulation of AGG/CIP/SSIP species on electrochemical performance and rule out accidental experimental results, Raman spectroscopy, low-temperature Na||Na symmetric cell and Na||HC half-cell tests on electrolytes with varied anion ratios (1:9, 3:7, 7:3, 9:1) at a fixed total salt concentration of 1 M were conducted (Supporting Information S1: Figures S36–S38). The results demonstrate that electrolytes with excessive PF_6^- generate abundant SSIP structures, leading to high Na^+ desolvation barriers, rapid capacity decay, and severe voltage fluctuations. In contrast, high OTF^- content produces excessive AGG, weakening the electrolyte's oxidative stability and aggravating the dissolution of transition metals from the cathode. These findings confirm that the 4:1 M ratio (HE electrolyte) balances the competitive coordination strength between the two anions, optimizes the distribution of AGG/CIP/SSIP, and achieves a favorable compromise between low desolvation energy and outstanding sodium storage performance under low-temperature environments.

4 | Conclusions

In summary, this work presents a dual-salt electrolyte strategy that enhances the sodium storage performance and temperature adaptability of hard carbon anodes by strategically balancing strongly (OTF^-) and weakly (PF_6^-) coordinating anions. High-throughput computational screening identified NaOTF and NaPF₆ as optimal salts when paired with the G2 solvent. Through combined molecular dynamics simulations, spectroscopic analysis, and DFT calculations, we demonstrate that this electrolyte design accelerates Na^+ transport kinetics, moderates the excessively strong Na^+ – OTF^- coulombic interaction, and optimizes the free-to-bound solvent ratio to enable rapid desolvation. Simultaneously, the formulation promotes the formation of a robust, homogeneous, and fluorine-rich SEI, significantly improving interfacial charge-transfer kinetics. As a result, Na||HC cells employing this electrolyte achieve a specific capacity of 78.4 mAh g^{-1} at an ultrahigh rate of 5 A g^{-1} at room temperature. At -30°C and 0.5 A g^{-1} , the cell maintains 77% capacity retention after nearly 2600 cycles, with an initial coulombic efficiency of 84.02%. The system also demonstrates stable high-rate operation at 60°C . Based on the HE electrolyte, full cells and pouch cells assembled with an HC anode and a commercial NFPP cathode were successfully charged and discharged at -20°C , demonstrating their potential for commercialization. This study demonstrates that rational solvation structure engineering based on anion coordination equilibrium offers a promising and versatile

strategy for interfacial design in dual-salt electrolyte systems, paving the way for high-performance sodium-ion batteries with wide-temperature operating capability.

Author Contributions

Mingxing Zhang: formal analysis, investigation, methodology, visualization, writing – original draft. **Tengfei Jiang:** formal analysis, investigation, methodology. **Fuang Liu:** formal analysis, visualization. **Huang Zhang:** conceptualization, project administration, supervision, writing – review and editing. **Saisai Qiu:** data curation, formal analysis, software. **Jian Wang:** data curation, validation, visualization. **Hongxu Qu:** data curation, formal analysis. **Jingxuan Wang:** formal analysis, visualization. **Sailei Shao:** validation, visualization. **Minghua Chen:** funding acquisition, project administration, supervision, writing – review and editing. **Huihua Li:** conceptualization, funding acquisition, project administration, supervision, writing – review and editing.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

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