

Dual-Polyhedral Distortion for Low-Cost Amorphous Halide Electrolytes with Improved Ionic Conductivity

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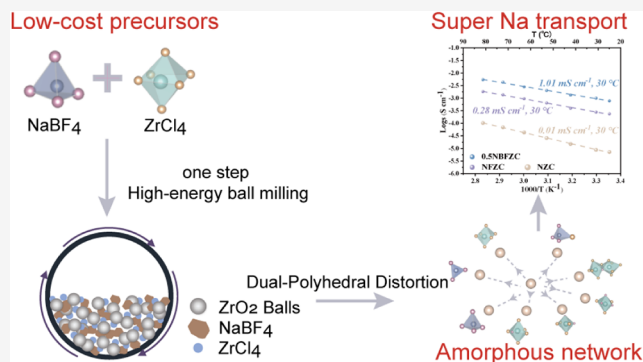


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ABSTRACT: Amorphous halide solid electrolytes (AHSEs) have emerged as promising candidates for high-performance all-solid-state Na batteries (ASSNBs) owing to their balanced comprehensive performance. However, rational design principles assisting the precursor selection are still limited for developing low-cost Na-based AHSEs with improved ionic conductivity. Herein, a series of low-cost AHSEs, $x\text{NaBF}_4\text{--ZrCl}_4$ ($x = 0.3, 0.5, 1$, and 2), were synthesized via a one-step mechanochemical process. Competitive coordination between the Zr^{4+} and B^{3+} cations under mechanochemical activation is proposed to promote the rearrangement of F^- and Cl^- anions within the halide framework. The resulting dual-distorted polyhedral coordination facilitates the formation of long-range disordered structures that are highly favorable for isotropic Na^+ transport, exhibiting a high Na^+ ionic conductivity up to 1.01 mS cm^{-1} at 30°C with excellent oxidative stability of 4.33 V vs Na^+/Na . When assembled into all-solid-state cells, the $0.5\text{NaBF}_4\text{--ZrCl}_4$ electrolyte enables stable cycling between 2.5 and 4.2 V with a capacity retention of 71.5% after 400 cycles at 0.2 C rate. This work provides a novel design paradigm for AHSEs and highlights the promising potential of high-performance ASSNBs.



1. INTRODUCTION

Lithium-ion batteries (LIBs) currently dominate the energy-storage landscape, owing to their high energy density and well-established industrial ecosystem. However, the uneven distribution of lithium resources and volatile lithium prices pose critical constraints for large-scale and sustainable deployment, spurring the exploration of alternative energy storage technologies.¹ As a result, Na-ion batteries have emerged as a promising candidate due to the natural abundance, low cost, and high compatibility with existing LIB manufacturing infrastructure.^{2,3} Particularly for large-scale energy storage applications, the growing demand for higher energy density⁴ and safety⁵ has drawn significant attention to all-solid-state Na batteries (ASSNBs),^{6,7} where the solid electrolytes (SEs) serve as the core component determining the practical performance.

Compared with various solid electrolyte systems, including polymers, sulfides, oxides, etc., halide-based electrolytes have attracted increasing interest due to their comprehensive properties on the ionic conductivity, oxidative stability, and favorable mechanical deformability, rendering them promising candidates for practical ASSNBs.^{6,8–12} Despite these merits, their room-temperature ionic conductivity, especially for the Na-based system, is still unsatisfactory, highlighting the continuous requirement to further accelerate the Na^+ trans-

port. Within the theoretical framework established for crystalline fast-ion conductors, favorable Na coordination environments, enlarged ion-migration bottlenecks,¹³ flat energy landscape,¹⁴ and mixed-anion local environments^{15,16} have been identified as effective structural strategies for achieving fast Na-ion conduction. Beyond these crystalline design principles, amorphization has been widely recognized as another promising route to enhancing the ionic conductivity of Na-based halide solid electrolytes. The formation of amorphous structures, often achieved through coordination modulation, induces local structural distortion and, ultimately, long-range disorder. Such structural features can reduce migration barriers, broaden ion transport pathways, and suppress crystallographic bottlenecks.¹⁷ In addition, amorphization can homogenize the energy landscape, increase the diversity of accessible diffusion sites, and mitigate grain-boundary resistance, thereby offering a viable route to

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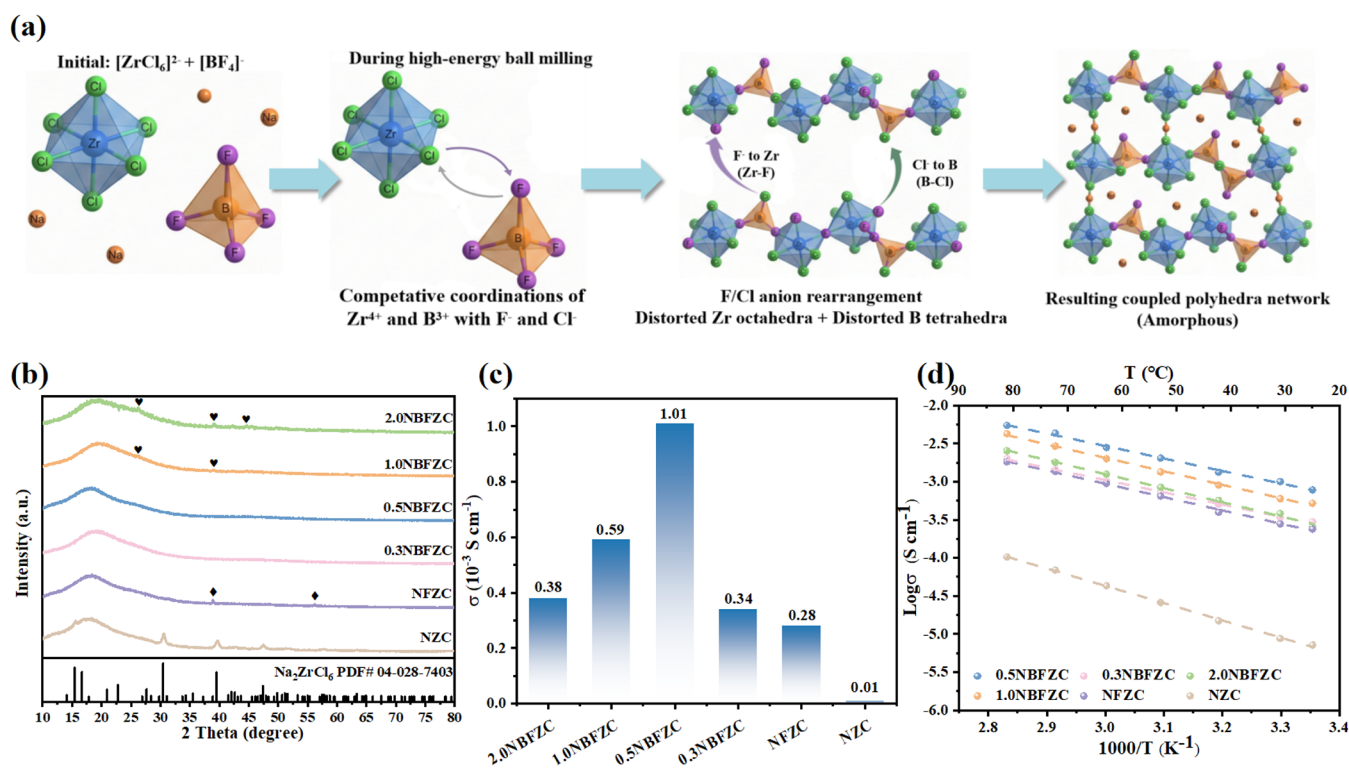


Figure 1. (a) Schematic illustration of the proposed formation of dual-distorted coordination polyhedra, possibly involving dynamic competitive coordination of halide anions with the central cations during the mechanochemical process. (b) XRD patterns of synthesized NZC, NFZC, and $x\text{NBFZC}$ ($x = 0.3, 0.5, 1.0$, and 2.0) powders. The heart and diamond symbols represent NaBF_4 and NaF , respectively. (c) The ionic conductivities of NZC, NFZC, and $x\text{NBFZC}$ ($x = 0.3, 0.5, 1.0$, and 2.0) at 30°C . (d) The Arrhenius plots of ionic conductivities of NZC, NFZC, and $x\text{NBFZC}$ ($x = 0.3, 0.5, 1.0$, and 2.0).

substantially improve the ionic conductivity of Na-based halide solid electrolytes.^{18–21}

Recently, numerous AHSEs have been reported with improved ionic conductivities compared with crystalline frameworks. Several studies attribute the glassy network formation to the interactions between the sodium salts and metal halides that exhibit Lewis acidity,^{22,23} while some other reports proposed that certain metal halides, by virtue of their van der Waals solid character, promote salt dissociation and thereby favor the development of an amorphous phase.²⁴ A further strategy involves deliberate introduction of heteroatoms into the host framework to perturb the originally ordered lattice and induce structural disorder. For example, oxygen can be introduced into halide-based systems either by employing oxygen-containing precursors or by adding external oxygen sources during synthesis to participate in ion-exchange processes, thereby promoting the formation of an amorphous phase.^{15,25–29} Nitrogen doping has also been suggested as another option to trigger amorphization by modulating local cation–anion coordination environments.^{30,31} In addition, the control of synthetic process such as extending the ball milling time³² or introducing a quenching step upon the calcination³³ can also effectively suppress crystallization and promote the formation of amorphous phases. However, despite these advances and the increasingly mechanistic interpretations of the current material design and synthesis approaches, the most reported Na^+ conductivity values still fall into the range of only 10^{-6} – $10^{-4} \text{ S cm}^{-1}$. On the other hand, although some doped elements such as Ta and Nb have been proven to obtain superior ionic conductivity even over $4 \times 10^{-3} \text{ S cm}^{-1}$, the ultrahigh cost and moderate high-voltage stability of the Ta or

Nb-containing materials still limit the scalability and practicability.³⁴ As a result, low-cost and high-performance AHSEs motivated by effective design strategies are still urgently required for the development of ASSNBs.

Here, we propose a series of novel amorphous halide solid electrolytes (AHSEs), $x\text{NaBF}_4\text{–ZrCl}_4$ ($x = 0.3, 0.5, 1$, and 2). During the mechanochemical activation, the Zr^{4+} and B^{3+} centers are proposed to compete for coordination with the F^- and Cl^- anions, which can promote the rearrangement of F^- and Cl^- from the original $[\text{BF}_4]^-$ tetrahedra and the $[\text{ZrCl}_6]^{2-}$ octahedra, respectively, and their incorporation into dual-distorted Zr- and B-centered polyhedral motifs within the halide frameworks as $[\text{ZrCl}_{6-x}\text{F}_x]^{2-}$ ($0 \leq x \leq 6$) and $[\text{BF}_{4-n}\text{Cl}_n]^-$ ($0 \leq n \leq 4$). These structural motifs could be associated with the formation of a long-range amorphous network and efficient isotropic Na^+ conduction (Figure 1a). Optimally, the $0.5\text{NaBF}_4\text{–ZrCl}_4$ (0.5NBFZC) shows the best ionic conductivity of 1.01 mS cm^{-1} at 30°C and high oxidative stability of 4.33 V vs Na^+/Na . When integrated into ASSNBs paired with $\text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}$ (NVOPF) cathode and $\text{Na}_{15}\text{Sn}_4$ anode, the 0.5NBFZC electrolytes enable stable cycling with over 70% capacity retention after 400 cycles at 0.2 C . Moreover, the cost of this electrolyte is much lower compared to most of the reported halide-based SEs, indicating the great potential of future commercialization. This work provides a rational strategy for designing high-conductive AHSEs through polyhedral distortion, facilitating the development of high-performance ASSNBs.

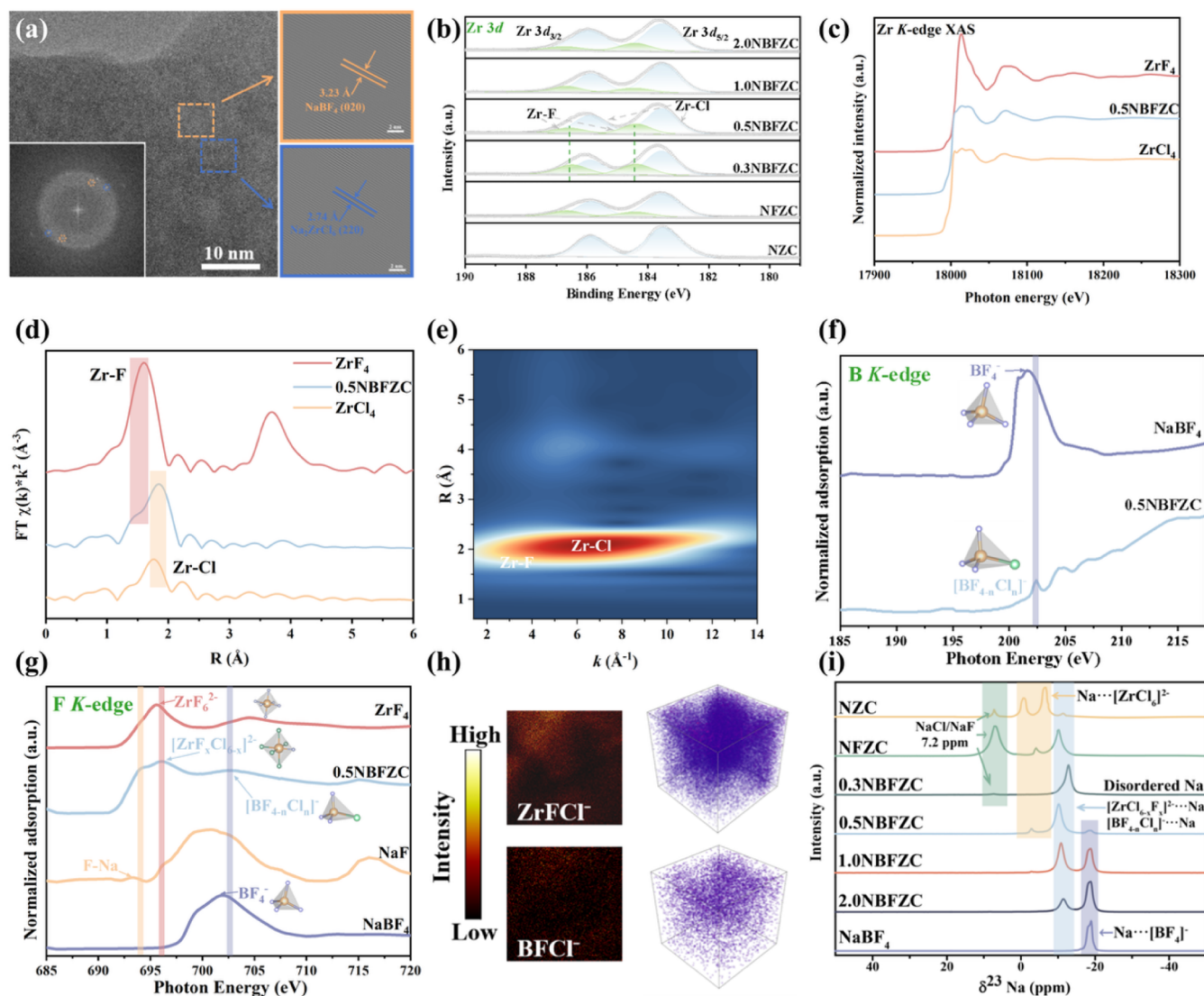


Figure 2. (a) cryo-TEM images of 0.5NBFZC, an FFT analysis on the entire image (inset), and an IFFT analysis of the orange- and blue-selected regions in the image on the left. (b) The deconvoluted Zr 3d XPS spectra of NZC, NFZC, and xNBFZC ($x = 0.3, 0.5, 1.0$, and 2.0). (c) Zr K-edge XANES spectra of ZrF_4 , ZrCl_4 , and 0.5NBFZC, showing distinct absorption edge positions and white-line intensities associated with different Zr coordination environments. (d) k^2 -weighted Fourier-transformed (FT) EXAFS spectra of 0.5NBFZC, ZrF_4 , and ZrCl_4 . (e) Wavelet transform EXAFS maps for 0.5NBFZC. (f) B K-edge XAS spectra of the 0.5NBFZC and NaBF_4 (reference material). (g) F K-edge XAS spectra of the 0.5NBFZC and ZrF_4 , NaF , NaBF_4 (reference material). (h) The TOF-SIMS analysis and 3D views of ZrFCl^- and BFCl^- fragments in 0.5NBFZC. (i) The ^{23}Na MAS NMR spectra of NZC, NFZC, and xNBFZC ($x = 0.3, 0.5, 1.0$, and 2.0).

2. RESULTS AND DISCUSSION

2.1. Synthesis and Electrochemical Properties of x-NBFZC

The $x\text{NaBF}_4\text{-ZrCl}_4$ (xNBFZC) samples with varying salt contents were synthesized by directly mixing the raw materials NaBF_4 and ZrCl_4 without any pretreatment, followed by high-energy ball milling at predetermined molar ratios ($x = 0.3, 0.5, 1.0$, and 2.0). The classical Na_2ZrCl_6 (NZC) sample was prepared from a stoichiometric mixture of NaCl and ZrCl_4 at 2:1 as reported.³⁵ Similarly, the NaF-ZrCl_4 (NFZC) is obtained by substituting NaF for NaCl and mixing it with ZrCl_4 at the corresponding stoichiometric ratio. The structures and phase compositions of the six halide-based SEs were characterized by X-ray powder diffraction (XRD). All the samples were protected with a polyimide (Kapton) tape to prevent air degradation during the measurement. The XRD analysis of NZC indicates that it still adopts the classical

trigonal phase structure with a space group of $P\bar{3}m1$ (Figure 1b).³⁶ The diffraction pattern of NFZC exhibits characteristic features of an amorphous phase, but the peaks corresponding to residual NaF are also observed, which is consistent with previous reports.³⁵ The diffuser diffraction features of the xNBFZC samples indicate the presence of a predominant amorphous fraction. Notably, when the NaBF_4 content exceeds $x = 1.0$, additional sharp diffraction peaks attributable to residual crystalline NaBF_4 can be clearly identified, suggesting incomplete incorporation of excess NaBF_4 into the amorphous halide framework at higher addition contents.

The ionic transport properties of NZC, NFZC, and xNBFZC were evaluated by electrochemical impedance spectroscopy (EIS). The 0.5NBFZC shows the highest ionic conductivity of 1.01 mS cm^{-1} at 30°C , which is significantly higher than those of NFZC and NZC. This clearly demonstrates the synergistic contribution of B and F to

enhance the ionic conductivity (Figure 1c). The activation energies were calculated from the temperature-dependent Nyquist profiles and Arrhenius plots (Figure 1d, Table S1), and the 0.5NBFZC sample delivers a low activation energy of 0.32 eV. It is worth noting that the slopes of the curves for the several samples in Figure 1d do not appear to differ significantly, which suggests that the activation energy is not the primary factor influencing the ionic conductivity of these electrolytes.³⁷ The electronic conductivities of NZC, NFZC, and xNBFZC were determined using direct current (DC) polarization measurements (Figure S1), and the low room-temperature electronic conductivity of $\sim 10^{-10}$ S cm⁻¹ excludes the possibility of mixed ionic–electronic conduction.

Scanning electron microscopy (SEM) images of the 0.5NBFZC powder reveal that the particle size of the synthesized solid electrolyte is approximately 2–5 μ m. The corresponding energy-dispersive spectrometer (EDS) elemental mappings confirm the homogeneous distribution of Na, B, F, Zr, and Cl elements throughout the 0.5NBFZC electrolyte (Figure S2). Compared with NZC and NFZC, the 0.5NBFZC shows markedly reduced surface porosity and a substantially higher densification when cold-pressed into pellets at 400 MPa (Figure S3). This enhanced compressibility is expected to facilitate more efficient ion transport across grain boundaries and to improve solid–solid interfacial contact, thereby contributing to superior electrochemical performance. The atomic force microscopy (AFM) measurements further corroborate this observation. In contrast to NZC (6.2 GPa) and NFZC (3.3 GPa), the B-containing 0.5NBFZC sample exhibits a significantly lower average Young's modulus of 2.1 GPa (Figure S4), suggesting its good deformability.

2.2. Local Structural Analysis of Amorphous 0.5NBFZC

Although B–F is more stable than B–Cl, Zr⁴⁺ also prefers to coordinate with F⁻ compared to Cl⁻ according to the thermodynamic perspective. Therefore, upon mechanochemical activation, the disruption of the original [BF₄]⁻ and [ZrCl₆]²⁻ coordination environments may allow competitive reconstruction between the cationic units and the halide anions, accompanied by partial anion rearrangement and the formation of dual-distorted Zr- and B-centered polyhedral motifs in the halide ligands, conceptually illustrated as [ZrCl_{6-x}F_x]²⁻ (0 $\leq x \leq 6$) and [BF_{4-n}Cl_n]⁻ (0 $\leq n \leq 4$). This could also be preliminarily inspired by the hard–soft acid–base (HSAB) theory since Zr and B are both hard acids, while F and Cl are both hard bases, which could be used to roughly help the precursor selection to make the anion rearrangement more likely to occur. The Fourier transform infrared (FTIR) spectra also preliminarily confirms the presence of the relevant vibrational features in 0.5NBFZC. Compared with the reference compound NaBF₄, the characteristic [BF₄]⁻ peak at ~ 1100 cm⁻¹ exhibits an obvious splitting, which is consistent with the incorporation of Cl⁻ into the B-centered coordination environment (Figure S5).

To further verify the hypothesis and investigate the microstructures of the synthesized 0.5NBFZC, cryogenic transmission electron microscopy (cryo-TEM) was employed, with the EDS mappings also confirming the homogeneous distribution of the contained elements (Figure S6). As shown in Figure S7, the Fast Fourier transform (FFT) of the entire image area exhibits no distinct diffraction spots, indicating the presence of a highly amorphous phase, which is consistent with the XRD results. Meanwhile, the appearance of several FFT

rings with different radii in reciprocal space suggests the coexistence of multiple different disordered states within the 0.5NBFZC structure. However, a few weak diffraction streaks are also observed, implying that some short-range ordered domains are embedded within the predominantly amorphous matrix (Figure 2a). Inverse Fast Fourier transformation (IFFT) was performed on the blue and yellow regions marked in reciprocal space in Figure 2a. The lattice spacing extracted from the yellow region is 3.23 Å, slightly larger than that of the (020) plane of NaBF₄ (3.13 Å). The relatively enlarged interplanar spacing is arisen from the incorporation of Cl⁻ into the original [BF₄]⁻ regular tetrahedra, where the significantly larger ionic radius of Cl⁻ compared with F⁻ induces structural distortion. Similarly, the lattice spacing obtained from the blue region is 2.74 Å, which is slightly less than the spacing of (220) plane of Na₂ZrCl₆ (2.87 Å). When the more electronegative F⁻ enters the original [ZrCl₆]²⁻ regular octahedral sites and replaces Cl⁻, the resulting Zr–F bonds become highly polar due to the interaction between F⁻ and the strongly electropositive Zr⁴⁺. Moreover, the smaller ionic radius of F⁻ enhances its electrostatic attraction to Zr⁴⁺, leading to shorter Zr–F bond lengths compared with Zr–Cl. This substitution-induced contraction distorts the coordination polyhedra and consequently reduces the corresponding lattice spacing. X-ray photoelectron spectroscopy (XPS) measurements were also conducted for all prepared samples to clarify the chemical composition and coordination environments (Figure 2b). In the Zr 3d spectra of NZC, NFZC, and xNBFZC (x = 0.3, 0.5, 1.0, and 2.0), the peaks at 183.7 and 185.9 eV correspond to Zr 3d_{5/2} and Zr 3d_{3/2} associated with Zr–Cl bonding.³⁸ In contrast, two additional peaks at 184.5 and 186.7 eV appear in the spectra of xNBFZC and NFZC, which are attributed to the formation of Zr–F bonds.^{39,40}

To further investigate the local coordination environment of Zr⁴⁺, Zr K-edge X-ray absorption spectroscopy (XAS) was performed. As shown in Figure 2c, the X-ray absorption near-edge structure (XANES) spectra of 0.5NBFZC, ZrCl₄, and ZrF₄ exhibit pronounced differences in both absorption edge positions and white-line (WL) intensities. The WL feature at the Zr K-edge arises from the electric dipole transition from the Zr 1s core level to unoccupied Zr 4d states. ZrF₄ displays the highest absorption edge energy (18008.6 eV) along with the most intense WL feature, whereas ZrCl₄ exhibits the lowest edge energy (18002.0 eV) and the weakest WL intensity. This contrast originates from the higher electronegativity of F relative to Cl, which imparts a stronger withdrawal of electron density from Zr, thereby increasing the density of unoccupied Zr 4d states and shifting the absorption edge to higher energy. Notably, the 0.5NBFZC electrolyte falls between these two reference compounds in all of the above parameters, with an absorption edge position of 18002.7 eV and a moderate WL intensity, indicating that the local coordination environment of Zr in 0.5NBFZC is partially modified relative to ZrCl₄ while remaining less fluorinated than ZrF₄. This intermediate behavior signifies a mixed F/Cl coordination environment surrounding the Zr centers, consistent with the partial substitution of Cl⁻ ligands by F⁻ in the Zr-centered octahedra.

Extended X-ray absorption fine structure (EXAFS) analysis was employed to obtain more detailed information on the atomic-scale coordination environment. The first-shell coordination peak in the range of 0–4 Å in the k²-weighted Fourier-transformed EXAFS spectrum of 0.5NBFZC can be deconvoluted into Zr–F and Zr–Cl contributions (Figure

2d), indicating that both halogen species coordinate to the Zr centers and form a mixed Zr–F/Zr–Cl coordination environment. Complementary wavelet transform (WT) analysis of the k^3 -weighted EXAFS spectra enables direct identification of individual scattering paths, with Zr–F and Zr–Cl signals distinctly resolved at approximately 1.5 and 2.0 Å in R-space, respectively (Figure 2e). In addition, as shown in Table S2, quantitative fitting of the data was performed to obtain the coordination numbers of F and Cl around Zr, which are ~ 1.49 and ~ 4.47 , respectively, whose sum is close to 6. These results indicate that the amorphous matrix of 0.5NBFZC contains Zr-centered octahedra featuring mixed F/Cl coordination environments, formed through partial substitution of Cl^- ligands in the original $[\text{ZrCl}_6]^{2-}$ framework by F^- , yielding distorted $[\text{ZrCl}_{6-x}\text{F}_x]^{2-}$ structural units.

Synchrotron soft X-ray absorption spectroscopy (sXAS) was employed to further probe the chemical structures of the resulting SEs. As shown in Figure 2f, the B K -edge absorption peak of 0.5NBFZC shifts to higher energies compared with that of NaBF_4 , indicating that the B atoms no longer retain the original symmetric and saturated $[\text{BF}_4]^-$ coordination. This distortion is likely because when the F^- from the $[\text{BF}_4]^-$ partially enters the Zr coordination as illustrated by the Zr K -edge EXAFS results above, some displaced Cl^- from the original $[\text{ZrCl}_6]^{2-}$ units would also be likely to enter the coordination environment of B to form the distorted $[\text{BF}_{4-n}\text{Cl}_n]^-$ units to maintain the overall charge balance. These factors lead to a more polarized and less homogeneous electronic environment around B^{3+} , increasing the energy barrier for $1s \rightarrow 2p$ electronic transitions and causing the absorption edge to shift toward higher energies. In Figure 2g, the characteristic peak in the F K -edge of 0.5NBFZC also shows a noticeable shift from the peak in ZrF_4 at 695.6 eV associated with the $[\text{ZrF}_6]^{2-}$ octahedra.⁴¹ Due to the F/Cl mixed coordination of $[\text{ZrCl}_{6-x}\text{F}_x]^{2-}$ in 0.5NBFZC, the combined influence of F^- and Cl^- results in an asymmetric ligand field around Zr^{4+} . Cl^- induces uneven electronic shielding compared to the symmetric $[\text{ZrF}_6]^{2-}$ octahedra, causing nonuniform polarization and subsequently shifting the F K -edge peak toward higher binding energies. A similar shift is also observed when comparing the F K -edge of 0.5NBFZC with those of NaF and NaBF_4 . Compared with the free-ion-like, electron-rich F^- in NaF and the highly symmetric, tetrahedrally coordinated F^- environment in NaBF_4 , the F^- species in 0.5NBFZC participates in coordination with B^{3+} and Cl^- . This would enhance the polarization, contract the electron cloud, and increase the excitation energy required for electronic transitions. Multiple lines of evidence consistently indicate the presence of distorted polyhedral coordination units, specifically the $[\text{ZrCl}_{6-x}\text{F}_x]^{2-}$ octahedra and the $[\text{BF}_{4-n}\text{Cl}_n]^-$ tetrahedra.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) provides additional structural insight consistent with the proposed coordination motifs. The characteristic ionic fragments ZrFCl^- and BFCl^- are detected in 0.5NBFZC (Figure 2h). The spatial distribution of these fragments was analyzed by TOF-SIMS 3D depth profiling. The depth profiles and three-dimensional reconstructions of ZrFCl^- and BFCl^- fragments show detectable signals throughout the sputtering depth, suggesting the real-space presence of mixed-halide coordination environments with Zr and B distributed within the amorphous matrix.

To investigate the influence of the dual distorted polyhedral coordination on the Na^+ in the amorphous matrix, magic-angle spinning (MAS) solid-state nuclear magnetic resonance spectroscopy (ssNMR) was employed to probe the local chemical environments surrounding Na^+ in each sample. As shown in Figure 2i, the characteristic peaks at 7.2 ppm in NZC typically attributed to the NaCl impurities formed during synthesis, according to previous reports.⁴² Similarly, because halide anions provide comparable local chemical environments, the resonance at 7.2 ppm in the NFZC and 0.3NBFZC spectrum corresponds to Na atoms coordinated with NaCl or NaF.³⁵ The two peaks located at -0.72 and -6.8 ppm arise from Na^+ ions associated with the $[\text{ZrCl}_6]^{2-}$ octahedra in the trigonal NZC phase.⁴² Compared with the Na spectrum of NaBF_4 , the intensity and full width at half-maximum (fwhm) of the resonance at -18.8 ppm corresponds to Na^+ coordinated with $[\text{BF}_4]^-$ tetrahedra and increase with increasing x in xNBFZC, especially when $x \geq 1.0$, which is consistent with the XRD results. Notably, a broad and asymmetric peak centered around -11 ppm indicates the presence of a large population of Na^+ in highly distorted coordination environments,⁴³ such as distorted octahedra $[\text{ZrCl}_{6-x}\text{F}_x]^{2-}$ and tetrahedra $[\text{BF}_{4-n}\text{Cl}_n]^-$, consistent with the highly disordered nature of these amorphous electrolytes.

To further confirm the dominant contribution of amorphous Na^+ species to ionic transport, Lorentzian–Gaussian peak deconvolution was applied to the disorder-related Na^+ resonances in xNBFZC and NFZC (Figure S8).^{44,45} Typically, sharp Lorentzian features are indicative of fast Na^+ conduction, whereas broad Gaussian components correspond to slower Na^+ transport in anisotropic, disordered environments.⁴⁶ For 0.5NBFZC, the fraction of the Lorentzian component representing fast Na^+ transport is 78.1%, significantly higher than that of NFZC (49.1%). This result suggests that the proposed dual distorted polyhedral coordination, associated with competitive cation coordination and anion rearrangement, facilitates fast Na^+ transport and contributes to the high ionic conductivity (Figure S9).

Since charge carrier concentration is also an important factor affect the ionic conductivity, and different ratios of NaBF_4 in the xNBFZC samples would introduce different Na^+ concentration. In order to further confirm the primary contribution of the dual-polyhedral distortion compared to the Na^+ concentration, two samples, 0.5NaCl–ZrCl₄ (0.5NZC) and 0.5NaF–ZrCl₄ (0.5NFZC), were additionally synthesized. Their ionic conductivities at 30 °C were measured as 0.09 and 0.12 mS cm^{−1} (Figure S10), respectively. In addition, the conductivity of 1.0NBFZC (0.59 mS cm^{−1}) shown in Figure 1c is also higher than that of NFZC (0.28 mS cm^{−1}). According to these comparisons, it is reasonable to support that the proposed dual-polyhedral distortion contributes more to the enhancement of ionic conductivity for 0.5NBFZC compared to the Na^+ concentration.

2.3. AIMD Analysis of Coordination Structures and Diffusion Dynamics in Amorphous 0.5NBFZC

Ab initio molecular dynamics (AIMD) simulations were further performed to elucidate the complex local coordination characteristics of the amorphous 0.5NBFZC and the structural origin of its amorphization. The AIMD model also suggests that possible competitive coordination involving the two central cations, together with the rearrangement of F^- and Cl^- anions, may generate diverse $[\text{ZrCl}_{6-x}\text{F}_x]^{2-}$ and

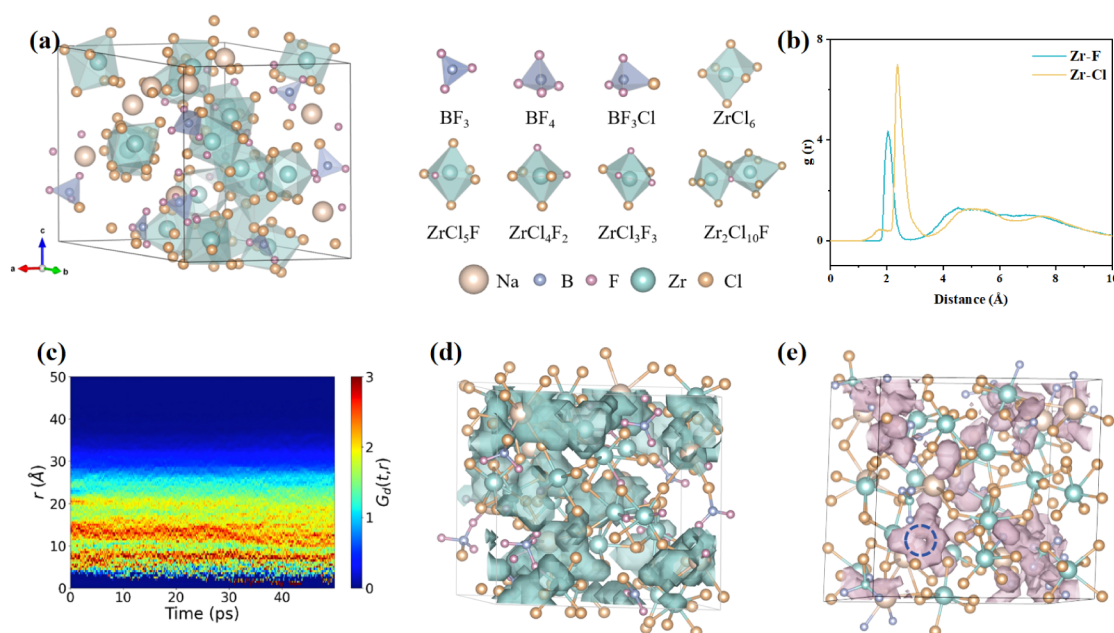


Figure 3. (a) Structure and partial coordination polyhedra of 0.5NBFZC obtained at 600 K. (b) The radial distribution function of the Zr atom interacted with F and Cl. (c) The van Hove correlation function of Na^+ dynamics in 0.5NBFZC. Isosurfaces of (d) Na and (e) F during AIMD simulations at 600 K.

$[\text{BF}_{4-n}\text{Cl}_n]^-$ polyhedra.⁴⁷ In addition, although it has not been experimentally validated directly, $[\text{Zr}_2\text{Cl}_{10}\text{F}]$ -type dimers and polymer-like motifs sharing F and/or Cl atoms were observed in the AIMD model (Figure 3a), implying that some F and Cl ligands serve as “fluorine or chloride bridges” that analogous to the “oxygen bridge” in oxyhalide electrolytes.¹⁵ The distortion of the coordination polyhedra was further corroborated by radial distribution function (RDF) analysis (Figure 3b).²³ Specifically, the Zr–F interaction exhibits a maximum at 2.03 Å, which is significantly shorter than the Zr–Cl distance of 2.30 Å, indicating stronger Zr–F bonding. This pronounced bond-length mismatch may contribute to the deformation of the $[\text{ZrCl}_{6-x}\text{F}_x]^{2-}$ coordination units.

The high Na^+ diffusivity in 0.5NBFZC was also confirmed through AIMD simulations. Figure S11a presents the mean square displacement (MSD) profiles of each atomic species in 0.5NBFZC from molecular dynamics simulations at 600 K.^{48,49} Among all elements, Na shows a markedly larger displacement than the others. Moreover, the MSD values for Na are comparable along different directions (Figure S11b), indicating three-dimensional isotropic diffusion of Na ions within the amorphous region. In the van Hove correlation analysis (Figure 3c), the rapid attenuation of the G_d peak further confirms the concerted migration of Na in 0.5NBFZC at 600 K from the perspective of Na-ion diffusion kinetics.⁵⁰ Furthermore, during the MD simulations, the Na isosurface density (Figure 3d) reveals three-dimensional Na-ion transport pathways in 0.5NBFZC across distorted $[\text{ZrCl}_{6-x}\text{F}_x]^{2-}$ octahedra, distorted $[\text{BF}_{4-n}\text{Cl}_n]^-$ tetrahedra, and through possible oligomeric motifs observed in the AIMD model. Notably, both F and Cl (Figure S12) also exhibit distinct isosurface features, in particular, the F isosurface (Figure 3e) shows numerous circular motifs, implying large-amplitude vibrational motion and segmental displacement of terminal halogen atoms within the distorted coordination units.

In short, by integrating extensive experimental characterization with molecular dynamics simulations, we propose that,

in the amorphous 0.5NBFZC, the central cations Zr^{4+} and B^{3+} can undergo competitive coordination with F^-/Cl^- , accompanied by anion rearrangement. Differences in atomic size and bond length are associated with the formation of distorted octahedra $[\text{ZrCl}_{6-x}\text{F}_x]^{2-}$ and distorted tetrahedra $[\text{BF}_{4-n}\text{Cl}_n]^-$, as well as possible oligomeric motifs observed in the AIMD model. These distorted polyhedral units favor the formation of long-range disordered structures. Furthermore, isosurface density maps of anions suggest large-amplitude vibrational motion and segmental displacement of terminal halogen atoms within the distorted coordination units, which dynamically broadens the Na^+ transport pathways and facilitates more isotropic ion diffusion through the amorphous framework.

2.4. Electrochemical Performance of ASSNBs Based on Amorphous 0.5NBFZC

The practical application of the amorphous 0.5NBFZC electrolyte was evaluated in ASSNBs. The electrochemical stability windows (ESW) of NZC, NFZC, and 0.5NBFZC were assessed with a linear sweep voltammetry (LSV) test at 0.1 mV/s; the oxidation onset voltage was ~ 4.23 V vs $\text{Na}^+/\text{Na}_{15}\text{Sn}_4$ (~ 4.33 V vs Na^+/Na) for 0.5NBFZC as shown in Figure 4a. Although the oxidative potential is lower than that of NFZC (Figure S13), it still indicates good compatibility with high-voltage cathode.

The all-solid-state cells employing the halide-based solid electrolytes were fabricated by cold-pressing the individual powder layers sequentially. High-voltage $\text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}$ (NVOPF) and $\text{Na}_{15}\text{Sn}_4$, without any additional treatments, were used as the cathode and anode, respectively. A sulfide-based solid electrolyte layer was inserted between the halide electrolyte and the anode to prevent undesirable reactions at their interface (Figure S14). The initial charge–discharge profiles of the all-solid-state cells cycled at 0.1 C rate (1 C = 130 mA g^{−1}) and 30 °C are shown in Figure 4b and S15. The ASSNBs incorporating the 0.5NBFZC electrolyte exhibits a high reversible capacity and an initial Coulombic efficiency

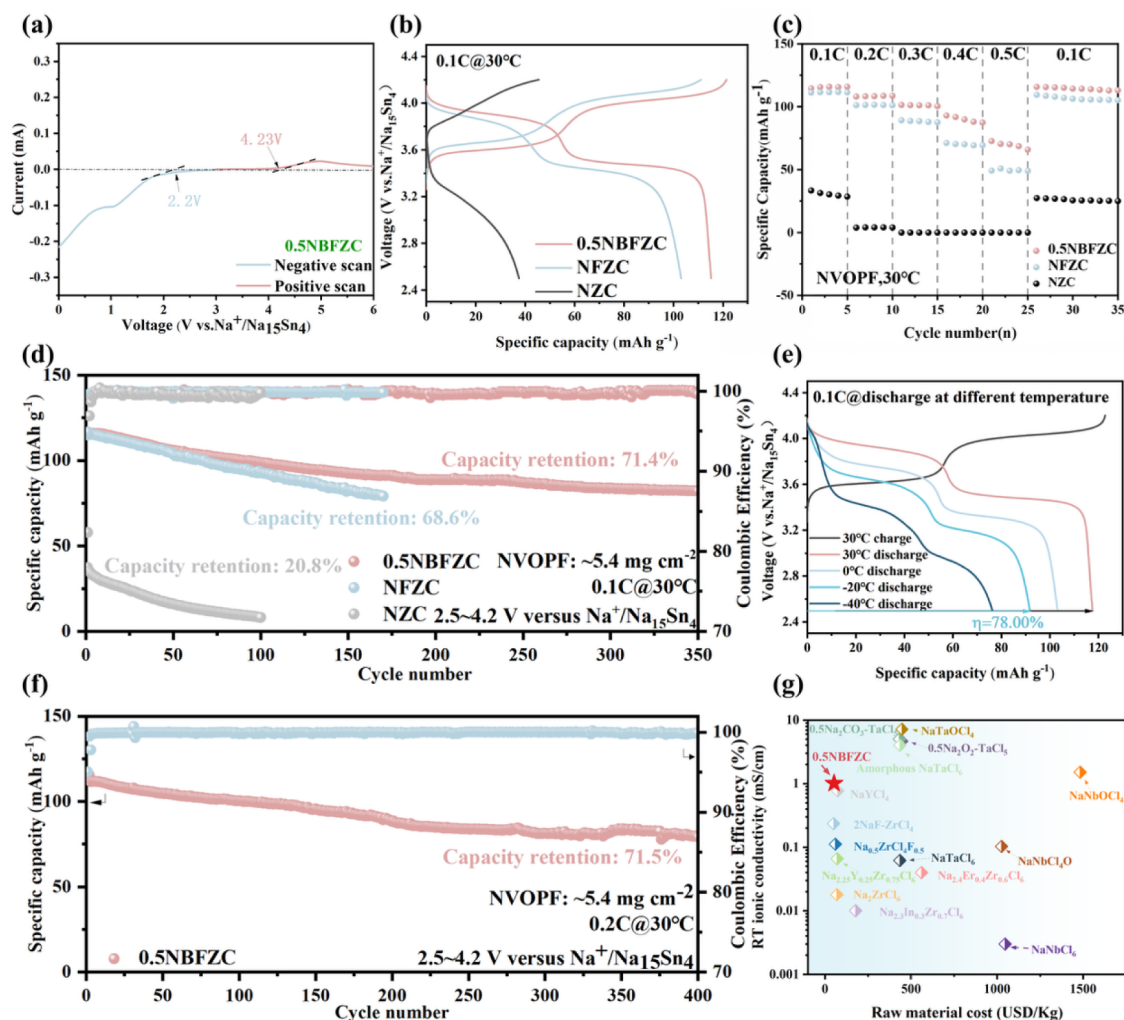


Figure 4. Electrochemical performance of ASSNBs. (a) The LSV curve of 0.5NBFZC at 30 °C. (b) The 1st cycle charge–discharge voltage–specific capacity profiles of NZC, NFZC, and 0.5NBFZC at 0.1 C rate. (c) The rate performance of ASSNBs with NZC, NFZC, and 0.5NBFZC halide electrolytes at 30 °C. (d) Cycling performance at 0.1 C rate of the ASSNBs with Na₃(VO)₂(PO₄)₂F (NVOF) and NZC or NFZC or 0.5NBFZC electrolytes. (e) Low-temperature discharge performance of ASSNBs-0.5NBFZC. (f) Cycling performance of ASSNBs-0.5NBFZC at 0.2 C rate and 30 °C. (g) Schematic comparison of the room temperature (RT) ionic conductivity and raw material cost between 0.5NBFZC and partially reported halide SSEs.

(ICE) of 117.6 mAh g^{−1} and 95.8%, respectively, outperforming the ASSNBs-NFZC (111.1 mAh/g, 92.7%) and significantly exceeding those of the ASSNBs-NZC (37.5 mAh/g, 82.4%). Assessment of the rate capability (Figure 4c) revealed that ASSNBs-0.5NBFZC was able to sustain reversible capacities of ~117.6, 108.2, 101.4, 93.0, and 72.7 mAh g^{−1} at 0.1, 0.2, 0.3, 0.4, and 0.5 C rates, respectively, which are superior to those of NFZC and NZC. The capacity is also able to be recovered when the rate turns back to 0.1 C rate. The 0.5NBFZC-based cell also exhibits excellent cycling stability between 2.5 and 4.2 V, with a capacity retention of 71.4% over 350 cycles at 0.1 C rate and 71.5% over 400 cycles at 0.2 C rate (Figure 4d and f). In addition, its low-temperature discharge performance was evaluated (Figure 4e). After being charged to 100% SOC at room temperature, the cell was transferred to low temperatures for discharge and still delivered 87.7% and 78.0% of its room-temperature capacity at 0 °C and −20 °C, respectively. Even under the extreme condition of −40 °C, the discharge capacity retention remains as high as 64.9% relative to that at room temperature.

The galvanostatic intermittent titration techniques (GITT) were performed to characterize the kinetics of the 0.5NBFZC-based cell during the first charge–discharge cycle. During the rest periods, the polarization generated under constant-current operation, including ohmic, activation, and concentration polarizations, can be effectively relaxed. Therefore, the terminal voltage at the end of each rest stage can be reasonably regarded as the thermodynamic equilibrium voltage, whereas the voltage drops occurring during the rest stage correspond to the overall polarization.⁴⁵ As shown in Figure S16, the ASSNBs incorporating 0.5NBFZC consistently maintain the lowest polarization among the three compositions, clearly demonstrating its kinetic advantage. Furthermore, the effective Na⁺ diffusion coefficients (D_{Na^+}) were calculated accordingly. During the charge–discharge process, D_{Na^+} falls within the range of 10^{−9} to 10^{−11} cm² s^{−1}. Across all voltage regions, the 0.5NBFZC-based cell exhibits significantly higher D_{Na^+} values compared with the other two counterparts, further confirming its good kinetics.^{36,45}

More importantly, as summarized in Figure 4g and Table S3–S4, we benchmarked a subset of reported halide-based solid

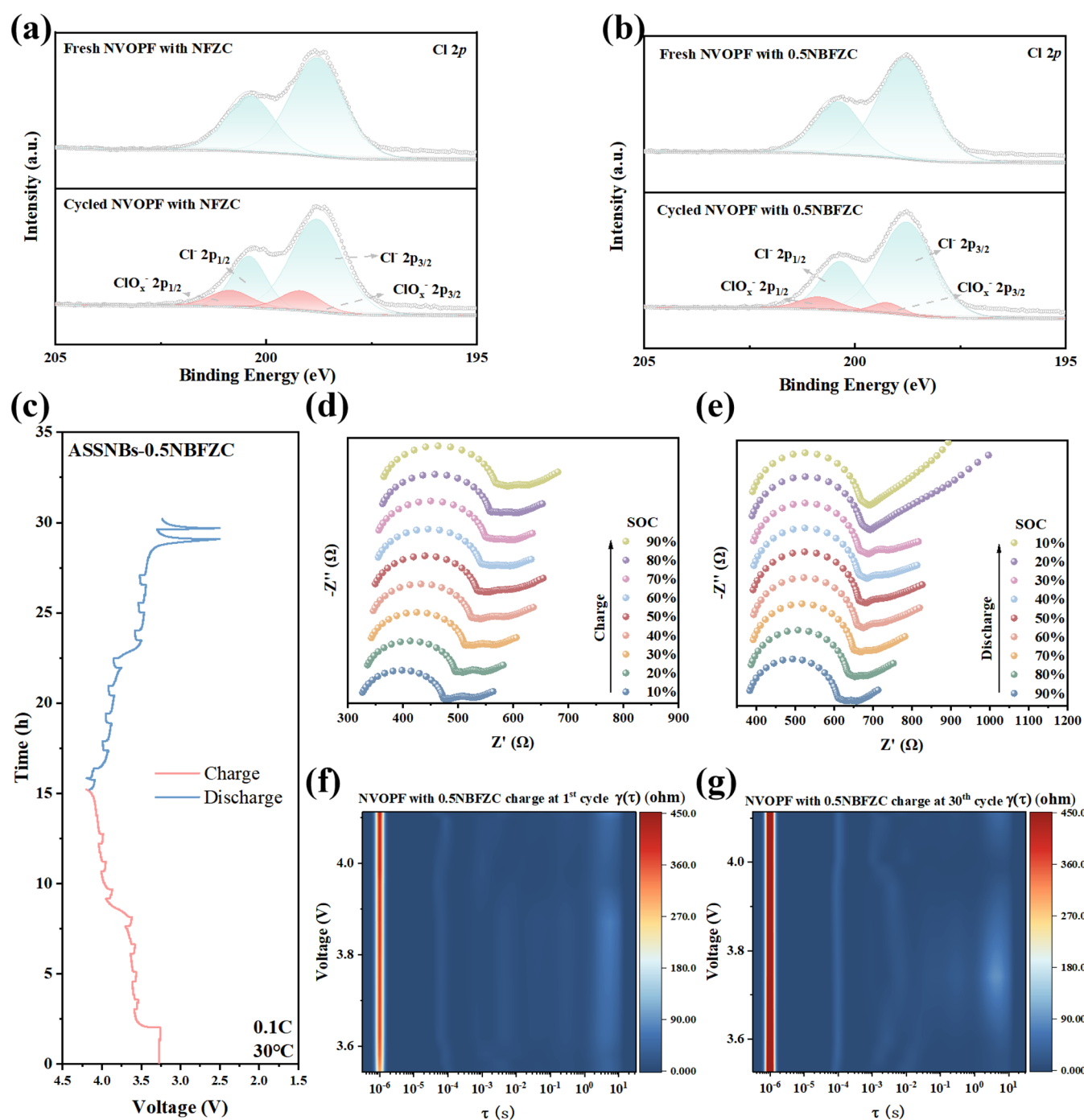


Figure 5. Investigate the origins of interface stability. The deconvoluted Cl 2p XPS spectrum of cycled NVOPF with (a) NFZC and (b) 0.5NBFZC. (c) Galvanostatic charge/discharge curve of the first cycle of ASSNB-0.5NBFZC. (d) The in situ EIS spectra of the cells recorded during the initial charge and (e) discharge process for the ASSNB-0.5NBFZC at 0.1C. 2D intensity color map DRT profile of the charging process of ASSNB-0.5NBFZC at the 1st cycle (f) and the 30th cycle (g).

electrolytes for Na-ion batteries in terms of their room-temperature ionic conductivity and precursor cost based on the model in the reported literatures.^{20,23,51} Notably, the associated raw material cost of 0.5NBFZC is only around 52.22 USD per kilogram, significantly lower than most of the reported halide-based electrolytes. The much higher cost of some electrolytes with superior ionic conductivity that heavily rely on expensive metals (e.g., Ta and Nb) highlights the favorable balance of 0.5NBFZC between high electrochemical

performance and low cost, thus demonstrating its strong potential for practical applications.

2.5. Thermodynamic and Kinetic Evolution of the Interface Before and After Cycling

To elucidate the thermodynamic and kinetic evolution of the interface in 0.5NBFZC-based ASSNB before and after cycling, XPS analyses were performed on the cycled composite cathodes to assess the extent of oxidative side reactions. Compared with NZC (30.4%) and NFZC (17.4%), only 9.7% of Cl⁻ was oxidized to ClO_x⁻ in the NVOPF cell employing

0.5NBFZC as the electrolyte (Figure 5a–b and S17–S18). The markedly lower fraction of ClO_x^- in the 0.5NBFZC-based composite cathode indicates substantially reduced parasitic reactions between 0.5NBFZC and NVOPF under high-voltage conditions.^{35,36,45} This result suggests that although the incorporation of F^- alone can suppress oxidative degradation against high-voltage cathodes, the synergistic effect of B and F provides an even more pronounced mitigation of interfacial side reactions.

The carrier-transport kinetics of the full cells before and after cycling were further analyzed by combining in situ EIS at different states of charge (SOC) (Figure 5c–e and S19–S20) with distribution of relaxation time (DRT) analysis. DRT analysis decomposes the total impedance derived from the *in situ* EIS data into individual relaxation processes distributed across distinct time scales, each corresponding to a specific electrochemical process. The resulting DRT signal provides a more intuitive representation of the evolution trends in the resistance contributions from each component. Compared with NFZC, the 0.5NBFZC-based cell exhibits significantly weaker peaks at 10^{-4} s both in the initial cycle and after 30 cycles, indicating a lower contact resistance (Figure S21).^{45,49} This suggests that 0.5NBFZC forms a more intimate solid–solid interface than NFZC, consistent with the SEM and AFM observations. Moreover, during both the first and 30th charge/discharge cycles, the mid- and low-frequency peaks of the 0.5NBFZC cell remain lower than those of NFZC, implying that the latter interface becomes severely diffusion-controlled and highly polarized, while the former remains predominantly limited by mild charge-transfer processes with unobstructed diffusion pathways.

After 30 cycles, the in situ EIS spectra of the 0.5NBFZC-based cell show a slight increase in Ohmic resistance relative to the first cycle (Figure 5f and g). However, a combined DRT analysis reveals reduced mid- and low-frequency peak intensities. This indicates that compared with the initial cycle, both the charge transfer and diffusion resistances decrease after electrochemical activation. In the low-frequency region during discharge, the peaks become narrower and shift toward shorter relaxation times, suggesting accelerated interfacial and diffusion kinetics.

Overall, these results demonstrate that 0.5NBFZC establishes a more stable cathode-electrolyte interface under high-voltage operation with substantially lower charge-transfer and diffusion resistances. The interfacial structure becomes even more stabilized upon moderate cycling activation, which accounts for the excellent rate capability and cycling stability of the 0.5NBFZC-based ASSNBs.

3. CONCLUSION

In conclusion, this work demonstrates a series of low-cost amorphous halide solid electrolytes through deliberate precursor selection and coordination tailoring. Within the proposed interpretation, competitive coordination of the cations Zr^{4+} and B^{3+} toward the halide ligands can promote the anion rearrangement and the formation of dual-distorted polyhedral motifs, namely Zr-centered octahedra coupled with B-centered tetrahedra. These structural motifs facilitate the formation of long-range disordered structures favorable for isotropic Na^+ transport. Using a one-step mechanochemical route, a series of low-cost $x\text{NaBF}_4\text{--ZrCl}_4$ electrolytes ($x = 0.3, 0.5, 1$, and 2) were synthesized, among which $0.5\text{NaBF}_4\text{--ZrCl}_4$ delivers the highest Na^+ ionic conductivity of 1.01 mS cm^{-1} at

30°C , good mechanical compliance, and excellent oxidative stability up to $4.33 \text{ V vs Na}^+/\text{Na}$. When implemented in an all-solid-state cell with an NVOPF cathode and $\text{Na}_{15}\text{Sn}_4$ anode, it enables stable cycling with over 70% capacity retention after 400 cycles at 0.2 C . These findings highlight a practical and generalizable route to engineer low-cost and high-performance AHSEs, which further advances the development of ASSNBs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.6c04535>.

Experimental section for electrolyte synthesis, materials characterization, electrochemical measurements, all-solid-state sodium battery assembly, and *ab initio* molecular dynamics (AIMD) simulations; supplementary figures and tables presenting structural and compositional analysis, morphology and elemental distribution, mechanical properties, Na-ion transport behavior, electrochemical stability, cell performance, as well as raw-material cost evaluation (PDF)

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Notes

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