



Synergistic optimization of ion kinetics and stability via gradient interphase engineering for high-performance aqueous Zn-ion batteries

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Received: 27 March 2026 / Revised: 14 April 2026 / Accepted: 28 April 2026 / Published date: 16 June 2026

ABSTRACT

Aqueous zinc-ion batteries (AZIBs) feature high safety, environmental compatibility, and low cost, being regarded as a promising candidate for sustainable energy storage. However, random spatial distribution of interfacial components deteriorates transport kinetics and interfacial stability, severely constrains the development of AZIBs. To address the issues, we herein introduce Carbomer 940 (CB) as a crosslinker for polyvinylidene fluoride (PVDF), forming a hybrid binder with enhanced viscosity, electronic conductivity, and ionic migration. Crucially, the binder enables gradient component distribution within interfacial film, achieving the collaborative enhancement of ion diffusion kinetics and electrode cycling stability. As a result, these cells using optimized hybrid binder exhibit the lifespan up to 1000 and 40,000 cycles with discharge capacity of 259.4 and 52.3 mAh·g⁻¹ at 1 and 10 A·g⁻¹, respectively. Furthermore, the hybrid binder further demonstrates its universality in lithium-ion and sodium-ion batteries. Therefore, the gradient interfacial design provides a synchronous solution for realizing long-cycle-life rechargeable batteries.

KEYWORDS

aqueous zinc ion batteries, hybrid binder, interfacial film, gradient component distribution, interfacial charge and transport

1 Instructions

To advance green energy development and achieve carbon neutrality, aqueous zinc-ion batteries (AZIBs) have emerged as promising candidates due to high theoretical capacity (820 mAh·g⁻¹) and volumetric capacity (5855 mAh·cm⁻³) of zinc metal [1–3], as well as its natural abundance, inherent safety, and low redox potential (−0.76 V vs. SHE). Consequently, cathode material development is pivotal, with research focusing on manganese-based compounds, Prussian blue analogs, organic materials, conversion materials, and vanadium-based materials [4]. Among these, vanadium-based cathodes attract particular interest due to their tunable crystal structures, multi-electron redox capability, and high electrochemical performance [5, 6]. However, critical challenges persist: strong electrostatic interactions between Zn²⁺ and vanadium oxide frameworks, by-product accumulation at interfaces, transition-metal dissolution, and sluggish Zn²⁺ diffusion

kinetics [7, 8]. These issues collectively hinder practical AZIB development.

Extensive strategies targeting cathode structural stability have been developed to pursue enhanced electrochemical performance, including defect introduction [9–11], organic/inorganic coatings [11, 12], and metal/non-metal ion doping [13–15]. Complementing these approaches, significant efforts focus on stabilizing the cathode/electrolyte interface through solvation structure modification [16, 17], hydrogen-bond network reinforcement [18–20], and novel electrolyte design to prolong AZIB lifespan [21–23]. Although these strategies have yielded obvious improvement in electrochemical performance, the modification strategy of binder and its interaction mechanism with active material have rarely been reported. Specifically, the different components in electrode are mixed and connected mainly by tenuous hydrogen bonding and van der Waals forces [24]. Poly (vinylidene fluoride) (PVDF) with excellent solubility in

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organic systems, served as a competitive binder for most cathode materials, demonstrating satisfactory thermal and chemical stabilities. Nevertheless, commercialization binder used with widespread acceptance of commercial products, PVDF still requires extensive efforts to revamp its demerits including insulating properties and low ionic conductivity, which could bring about additional Zn^{2+} migration barriers to induce sluggish charges conduction kinetics [25]. Besides those, as a long-chain organic molecule, the weak interaction through hydrogen bond and van der Waals forces between PVDF and other components could not provide adequate robustness for various components upon cycling to aggravate electrochemical performances [26].

Recent binder designs remain confined to enhancing adhesion or ionic conductivity [27, 28]. Critically, the key role of binder-induced component distribution in regulating interfacial charge/ion transport has devoted inadequate attention. In conventional PVDF-based cathode electrolyte interface (CEI) layers, random distribution of organic and inorganic phase induces uneven electric fields and ion diffusion barriers, accelerating capacity decay [29]. This knowledge gap motivates our strategy of architecting gradient interfacial films via molecular-level binder engineering.

Herein, we demonstrate that a hydrogen-bonded helical network between PVDF and Carboxyl (CB) programmatically drives gradient segregation of organic/inorganic components during cycling. Specifically, carboxyl-rich CB domains preferentially adsorb Zn^{2+} to form an ion-conductive outer layer, while the PVDF framework anchors F^- to construct an inner ZnF_2 -rich diffusion barrier. This multi-site crosslinking architecture establishes that spatially graded component distribution in interfacial film optimizes charge redistribution at interfaces and enhances ionic transport kinetics and structure steadiness (Scheme 1). Consequently, AZIBs using the hybrid binder achieve exceptional cyclability-retaining 73.3% capacity after 1000 cycles at $1 \text{ A}\cdot\text{g}^{-1}$ and sustaining 40,000 cycles at $10 \text{ A}\cdot\text{g}^{-1}$. Meanwhile, the hybrid binder allows the electrode to maintain stable performance over 2000 cycles, with capacities reaching 133.3 and $117.9 \text{ mAh}\cdot\text{g}^{-1}$ even when the mass loadings are as high as 5.72 and $7.49 \text{ mg}\cdot\text{cm}^{-2}$, respectively. In addition, the high-temperature tolerance has been significantly enhanced due to the presence of gradient interphase. More importantly, the improved cycling performance of lithium-ion batteries and sodium-ion batteries also demonstrates the broad universality for the hybrid binder. This interfacial engineering strategy simultaneously fulfills high-performance and sustainability objectives for next-generation energy storage.

2 Experimental

2.1 Synthesis of cross-linked PVDF-CB hybrid binder

The PVDF-CB hybrid binder was synthesized using an easy cross-linking method. Polyvinylidene difluoride (PVDF, Aladdin, $M_w = 1300,000$) and Carboxyl (CB, Macklin, 99%, $M_w = 10,000$) with a mass ratio of 1:0, 10:1, 2:10, and 3:10, respectively, were grinded for 2 h in mortar to obtain the PVDF-CB hybrid binder. In order to benefit the characterization and analysis, the binders in different CB contents were denoted as PVDF, 10%CB-PVDF, 20%CB-PVDF, and 30%CB-PVDF. Furthermore, the different binders powder needs to be dissolved in NMP before use with continuous stirring for 5 h to form a gelatinous liquid.

2.2 Preparation of the NaVO cathode

The $\text{Na}_2\text{V}_6\text{O}_{16}\cdot 3\text{H}_2\text{O}$ (NaVO), as cathode material, utilized in this

work are adopted from work previously reported by our group. In detail, $2.5 \text{ mmol V}_2\text{O}_5$ is dissolved in 30 mL deionized water and stirred for 1 h. Subsequently, 4 mL diluted hydrogen peroxide solution is added and stirred continuously for 1 h until the solution is dark red, and 3 mmol NaOH is further added and stirred further for 1 h, and when the solution is free of obvious bubbles, which is poured into 50 mL of reactor at 200°C for 24 h. After the hydrothermal reaction, the rubber state substance is dried for 10 h, and washed with deionized water and ethanol with several times until the liquid being filtered was clarified. The final orange-red powder obtained was the target product NaVO. The cathode electrodes are prepared by comprising 70 wt.% NaVO, 20 wt.% acetylene black, and quantifiable blended sol, which are mixed and well stirred up to 6 h in N-methyl-2-pyrrolidone (NMP) and cast onto a 12 mm stain steel (SS) current collector.

2.3 Electrochemical measurements

Zn foils with diameter of 16 mm , thickness of $100 \mu\text{m}$ as anode and glass fiber (GF/D-Whatman) as a separator were assembled into a CR-2016 type coin cell in open environment. Rate performance, long-term cycling performance at different current densities tests for Zn||NaVO cells using different binders were recorded on a LANHE system (CT 3002A, Wuhan, China). The cyclic voltammetry (CV) at various scan rates for Zn||NaVO cells were conducted on a CHI660E electrochemical workstation within 0.4 and 1.6 V (Chenhua, Shanghai). In addition, electrochemical impedance spectra (EIS) were measured on a CHI660C electrochemical workstation within 0.01 and $100,000 \text{ Hz}$ (Chenhua, Shanghai).

2.4 Materials characterization

Fourier transfer infrared (FT-IR) spectra for cathodes using different binders are recorded on a Bruker vertex70 spectrometer ranging from 400 to 4000 cm^{-1} . *In-situ* Raman spectra for cathodes using different binders are probed by Raman spectrometer of Via-Reflex optical spectrometer. X-ray photoelectron spectroscopy (XPS) measurements with electrodes using various binders in different etching depth are performed on a Thermo escalab 250Xi to elucidate species and chemical valence status of the elements. Images of electrodes using various binders in different states are presented by the Phenom ProX G6. The contact angles between the electrodes with different binders and the electrolyte were measured using the OCA25 contact angle meter. The zeta potential was measured using the ZS90 nanoparticle analyzer. The morphologies of cathodes materials are characterized by field emission scanning electron microscopy (SEM, JEOLJSM-7610FPlus). All HRTEM images are detect via Japanese JEOLJEM-2100 high-resolution transmission electron microscopy (TEM). Time of flight secondary ion mass spectrometry (TOF-SIMS, TOF5, Germany) is implemented to render the CEI components of electrode using 20% CB-PVDF. Inductively coupled plasma mass spectrometry (Thermo Fisher, iCAP RQplus) is carried out to measure vanadium element content on anode, cathode as well as separator after cycling for different binders. The crystal structure and phase of materials are tested in Bruker-D8A-A25 X-ray diffractometer and K_α -ray of Cu target as excitation source in 40 kV and 40 mA .

2.5 DFT calculations

Density functional theory (DFT) calculations are conducted using the Vienna *Ab initio* Simulation Package (VASP) code and

Perfectly Matched Bases Energies (PBE) exchange correlation functional. A plane wave basis set with an energy cutoff of 400 eV is used to represent the valence electrons with a Projector Augmented Wave (PAW) representation of the core electrons. The Brillouin zone (periodic boundary conditions) is sampled by $3 \times 1 \times 1$ k-points with the Monkhorst-Pack scheme for CB-PVDF and PVDF. The structure is optimized until the forces on all movable atoms below 0.01 eV/Å. Of which, the direction and energy convergence are reached within 10^{-5} eV/atom to calculate the binding energy (B.E.) of different polymers (PVDF, CB, and CB-PVDF) for water molecules, zinc ions and vanadium ions of different valence states, respectively.

3 Results and discussion

PVDF has been commonly utilized as a binder in electrode fabrication, however its inherent drawbacks deteriorate electrochemical performance during cycling. To address these limitations, CB polymer is introduced as a crosslinker due to its abundance of carboxyl groups (Fig.S1 in the Electronic Supplementary Material (ESM)). By establishing H-F correlation via the hydrogen bond between -COOH of CB and -F of PVDF, an innovative hydrogen-bond helix is architected through molecular cross-linking to reinforce chemical interactions among different components of electrode [30]. To reveal the intermolecular interaction differences between different polymers, the binding energy was determined via first-principles calculations based on DFT. Firstly, geometric optimizations for two interacting

PVDF molecules reveal that the hydrogen bond distance of H-F is 2.45 Å. However, the hydrogen bond distance of H-F interaction between CB and PVDF molecules undergoes a drastic reduction, reaching 1.92 Å. Concurrently, a new hydrogen bond interaction (H-O) emerges, with a distance of 2.35 Å (Figs. 1(a) and 1(b)). These results demonstrate that the introduction of CB shortens the inter-polymer distances and enhances the structural stability of binder. In addition, as illustrated in Fig. 1(c), the binding energies between PVDF-PVDF and PVDF-CB molecules are calculated to be -0.18 and -0.42 eV, respectively. This result indicates that the incorporation of CB molecule could enhance the adhesive properties of the binder itself by strengthening the intermolecular interactions among polymer chains.

In order to demonstrate the hydrogen bonding network modulation with the introducing of CB, the Fourier transform infrared (FTIR) spectroscopy (Fig. 1(d)) in 3000–4000 cm^{-1} was performed for the binders containing various CB contents to detect the alteration of hydrogen bond components. The O-H could be categorized into strong, moderate, and weak hydrogen bonds, located at 3440, 3550, and 3590 cm^{-1} , respectively [31]. The protruding region at 3440 cm^{-1} indicates an increased proportion of strong hydrogen bond, thus implying that the adhesiveness rises to strengthen the stability of different electrode components. To more intuitively observe the enhancement of electrode stability, SEM images of electrodes with varying CB loadings were acquired. As displayed in Fig. 1(e), the electrode using pure PVDF exhibits significant cracks, while 10% CB is incorporated, the number of surface cracks decreases. As the CB content increases to 20%, the

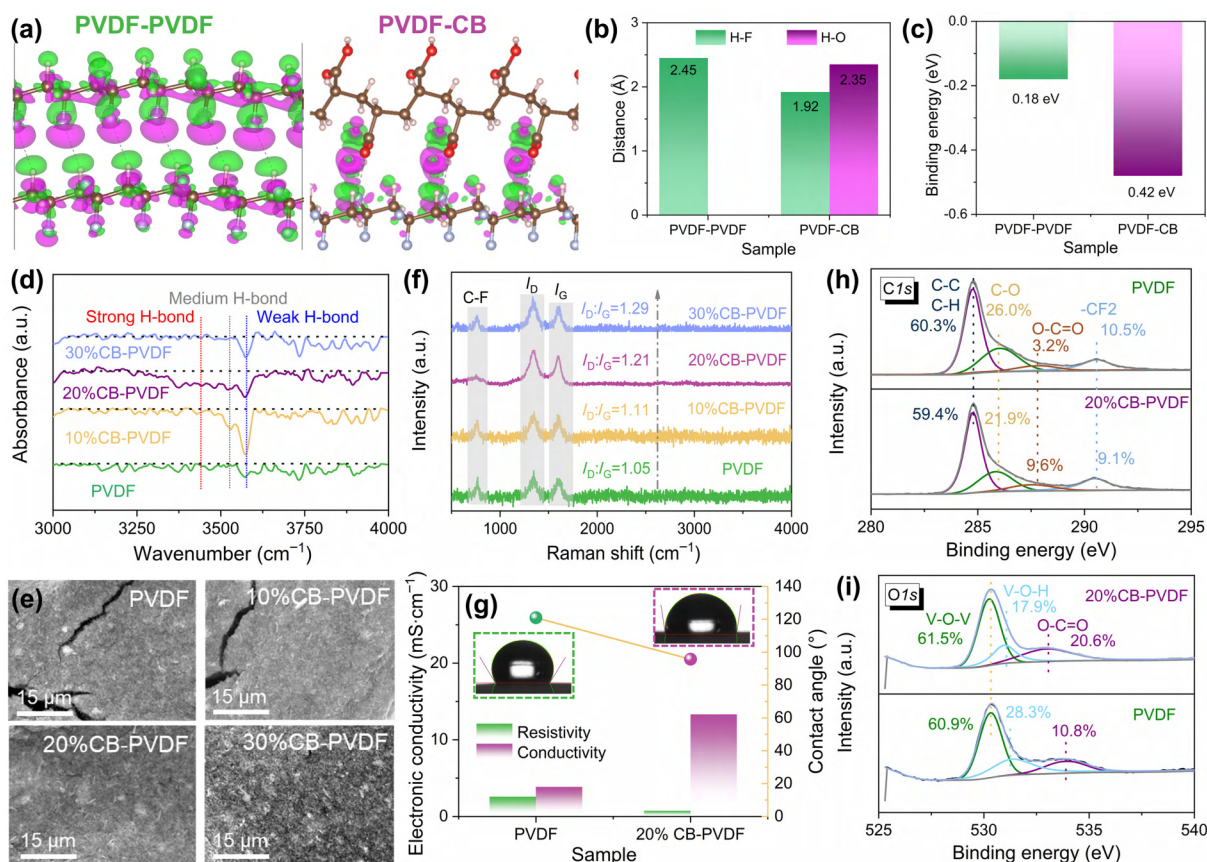


Figure 1 Molecular interactions and characterizations of CB-PVDF binders. (a) Charge density difference for PVDF-PVDF (2.2×10^{-4} e/Born³) and PVDF-CB (1×10^{-3} e/Born³) binders. (b) The hydrogen bond distances of corresponding groups in different polymers. (c) Binding energies for PVDF-PVDF and PVDF-CB binders. (d) Infrared spectra of electrodes with different CB contents. (e) SEM images of electrodes with different CB contents. (f) Raman spectra electrodes with different CB contents. (g) Electronic conductivity (left) and contact angles (right) of the electrode using PVDF and 20% CB-PVDF hybrid binder. (h) and (i) XPS spectra of C 1s and O 1s in electrodes using PVDF and 20% CB-PVDF binders, respectively.

electrode surface emerges as a crack-free and smooth morphology. When the CB content further ascends to 30%, distinct particle agglomeration occurs on electrode surface, resulting in an uneven topography. In addition, the stability of slurries on the collector with different CB contents was evaluated by sonicating them in electrolyte for 1.5 h (Fig. S2 in the ESM). It is noteworthy that the electrode using 20% CB-PVDF soaked electrolyte maintains thorough clarity, while sediments are observed to fall off from the electrodes with other CB contents.

In addition, the Raman spectra was performed to illustrate the different vibration mode of chemical bonds. D-band (1350 cm^{-1}) represents the defects in electrode, while G-band (1620 cm^{-1}) could be deemed as in-plane stretching vibrations of sp^2 hybridization of carbon atoms [32]. As revealed in Fig. 1(f), the I_D/I_G values are determined to be 1.05, 1.11, 1.21, and 1.29 for PVDF, 10%CB-PVDF, 20%CB-PVDF, and 30%CB-PVDF, respectively, unveiling the amorphous nature and low graphitization degree of carbon [33]. The increase of I_D/I_G values indicates that the electrodes could provide numerous active sites to regulate Zn^{2+} migration. Considering the increase in reactive groups, the contact angle measurement was conducted to evaluate the surface energy between electrolyte and electrodes containing PVDF and 20%CB-PVDF, respectively. As depicted in Fig. 1(g) (right), the contact angle decreased from 122° for pure PVDF to 98° for 20%CB-PVDF hybrid binder. Reduction of contact angle indicates that the appropriate CB increases the surface energy at electrode-electrolyte interface, thereby facilitating the zinc ions diffusion kinetics via enhancing the electrode wettability [34].

In addition to the improvement of ionic conductivity, electronic conductivity carries equal significance for energizing electrode activity. Therefore, the electronic conductivity of electrodes using PVDF and 20%CB-PVDF was probed by conducting four-probe resistivity tester and is shown in Fig. 1(g) (left). Based on electrode resistance at various locations (Fig. S3 in the ESM), the electronic conductivity of hybrid binder is determined to be nearly three times higher than that of pure PVDF, revealing a promising improvement in rate performance corroborated by Raman analysis results. Furthermore, the elemental composition and valence states on electrodes were detected by XPS. Regarding the XPS spectra of F 1s (Fig. S4 in the ESM), the signal peak of CF_2 shifts to a higher binding energy position by 0.16 eV, further suggesting the formation of a stronger hydrogen bond network in hybrid binder [35]. XPS survey spectrum of C 1s for electrodes using pure PVDF and 20%CB-PVDF are detected at 284.5, 285.7, 288.1 and 290.7 eV, which could be identified as C-C/C-H, C-O, O-C=O and $-\text{CF}_2$, respectively (Fig. 1(h)). The O-C=O group content in electrode using 20% CB-PVDF is increased to 9.5% from 3.2% by simulating the integrated area of different signal peaks [36]. While, the XPS high-resolution spectrum of O 1s for 20%CB-PVDF (Fig. 1(i)), sub-peaks at 530.3, 532.3 and 533.8 eV correspond to three different binding modes of V-O-V, V-O-H and O-C=O, respectively [37]. In the fitted signal peaks, it could be observed that the contents of O-C=O signal peak increase to 10.8% from 20.6% and shifts towards lower binding energy, confirming strengthened hydrogen bonding among different components.

To investigate the influence of PVDF, 10%CB-PVDF, 20%CB-PVDF, and 30%CB-PVDF hybrid binders on $\text{Na}_2\text{V}_6\text{O}_{16}\cdot 3\text{H}_2\text{O}$ (NaVO) cathode interface, high resolution transmission electron microscope (HRTEM) tests were adopted on NaVO cathode after 50 cycles using different binders. As offered in Fig. S5 in the ESM, the NaVO cathode using pure PVDF exhibits a pure inorganic

CEI layer with a thickness of 15 nm. After introducing 10% CB, lattice fringes of represented inorganic substances and amorphous morphologies represented organic substances appear with disorderly lattice fringes and inhomogeneity amorphous morphologies. As the CB content increases to 20%, a distinct layered structure appears on NaVO cathode. The innermost layer adjacent to the cathode comprises inorganic substances with lattice fringes; the middle layer predominantly features amorphous inorganic morphologies; and the outermost layer exhibits faint lattice fringes, collectively forming a gradient CEI with organic and inorganic components. Ultimately, with 30%CB addition, the lattice fringes distribution and amorphous morphology show similarities to those of NaVO in the electrode containing 10%CB, displaying an inhomogeneous distribution. Nevertheless, a marked distinction emerges: the edge surface exhibits unevenness and single lattice fringe pattern owing to excessive CB triggering the decomposition of C-F bonds in PVDF.

As revealed in Fig. 2(a), HRTEM image for NaVO cathode using pure PVDF manifests a bare inorganic CEI layer with a thickness of 15 nm on cathode. In order to discriminate substance species in inorganic CEI layer, the lattice stripes were partially magnified using an HRTEM image. The lattice fringes could be matched to (100) and (101) crystal planes of ZnO as well as (101) and (105) crystal planes of ZnS based on the characteristic lattice spacing (Figs. 2(a₁-a₄)). In striking contrast, evidenced by the HRTEM image of NaVO cathode using 20%CB-PVDF (Fig. 2(b)), the CEI with an average thickness of 15 nm is observed on cathode, ensuring the superior stability of NaVO structure by structure expansion [22]. The components for gradient CEI were discriminated to be ZnF_2 , ZnO and inorganic materials containing carbon groups by quantifying the stripe spacing (Figs. 2(b₁-b₄)).

In order to clarify the variability in coordination environments among different elements within distinct CEI layers, the depth-resolved XPS test was conducted for electrodes (Fig. S6 in the ESM). In the XPS spectra of S 2p, the profiles could be fitted to three signal peaks labelled as ZnS, SO_3^{2-} and SO_4^{2-} , respectively [38]. In contrast, the electrode using the hybrid binder demonstrates a consistently elevated integration ratio of SO_3^{2-} content as the etching depth increases (Fig. S2(c) in the ESM). The signal peaks of SO_4^{2-} remain continuously weaker than those using the PVDF binder. The O 1s is referred to three signal peaks assigned to V-O-V, V-O-H and O-C=O, respectively [39]. Based on the area ratio, the O-C=O in PVDF originates from Cotchin black, and the higher integral area in the hybrid binder could be attributed to the introduction of CB in the 20%CB-PVDF hybrid binder. Of particular interest is that the appearance of SO_4^{2-} signal peak at 0 nm on NaVO cathode using PVDF implies the by-product $\text{Zn}_4\text{SO}_4(\text{OH})_6\cdot n\text{H}_2\text{O}$ (ZHS) generation, in conjunction with the S 2p analysis results. In XPS spectrum of Zn 2p, it could be distinctly distinguished that the gradual decrease in ZnO content is accompanied by the increase of etching depth [40]. For the F 1s spectrum, two signal peaks located at 692.3 and 684.8 eV correspond to the ZnF_2 and C-F, respectively (Fig. S2(d) in the ESM) [41]. The hybrid binder electrode exhibits significantly elevated ZnF_2 concentrations throughout all etching depths compared to PVDF.

Subsequently, Time of flight secondary ion mass spectrometry characterization was performed using a Ga^+ ion beam to analyze the distribution of different species in CEI (Fig. S7 in the ESM). After etching the CEI layer on NaVO cathode surface using PVDF for 750 seconds, the total 3D mapping of PVDF (Fig. 2(e) in the ESM) unfolds that it is composed of ZnF_2 and ZnS, with ZnO

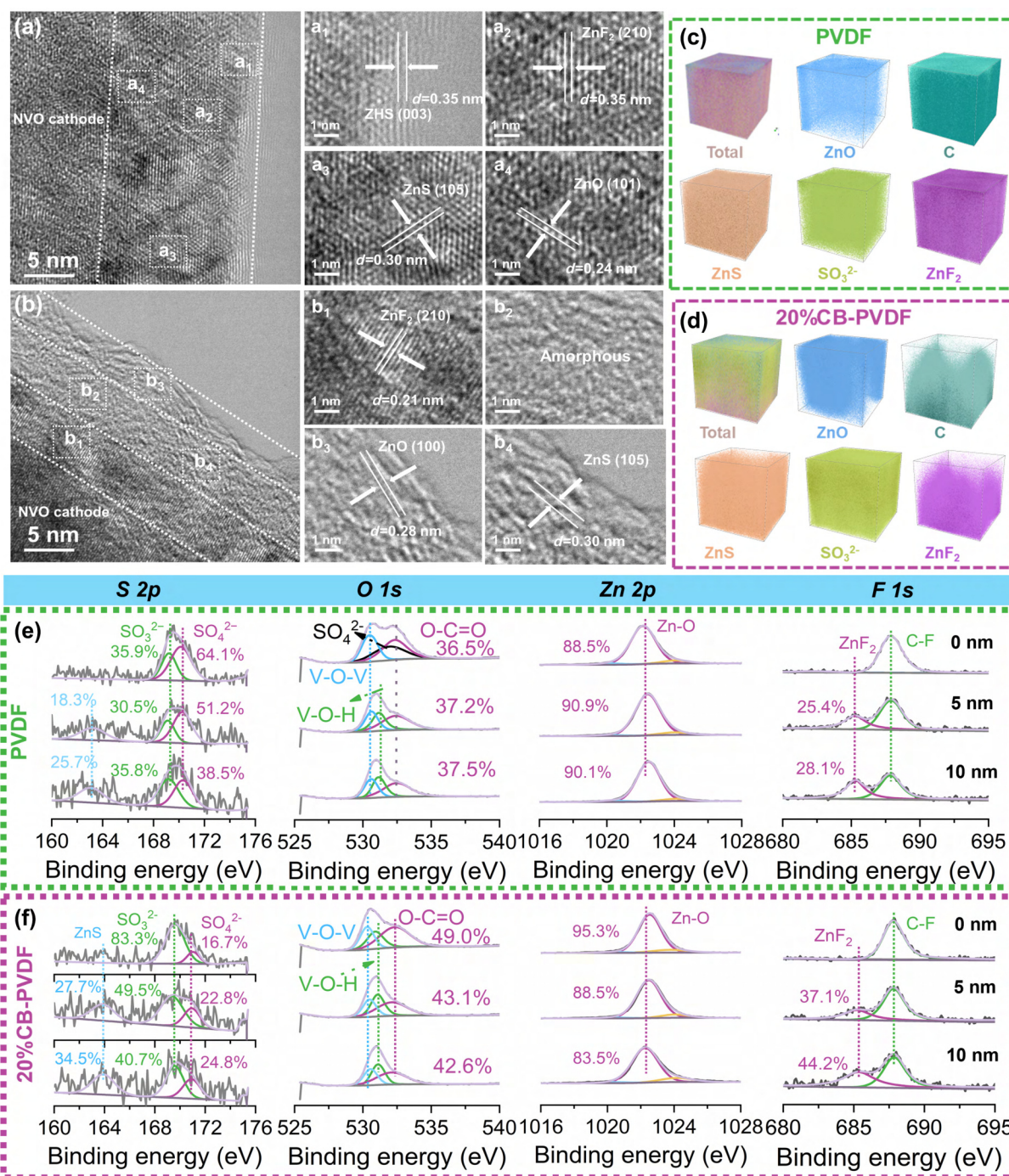


Figure 2 Spatial components distribution of gradient CEI. (a, b) HRTEM images cycled electrodes using PVDF and 20%CB-PVDF, respectively. (c, d) 3D visualization of TOF-SIMS for different groups. (e, f) XPS depth profiles of S 2p, O 1s, Zn 2p and F 1s for cathodes cycled.

tending to be at the topmost layer. For electrode surface using the hybrid binder, the overall 3D mapping (Fig. 2(f)) reveals that the surface is entirely composed of SO_3^{2-} , with ZnF_2 in the bottom layer. Although ZnO in both electrodes exhibits a high surface concentration that gradually decreases as the etching depth increases, the electrode using the hybrid binder manifests a higher surface concentration of ZnO, with a more distinct gradient change as the etching depth increases. Additionally, the distribution of ZnF_2 and carbon-based substances tends to be accumulated in inner layer, and their concentrations continue to increase with increasing etching depth without significant attenuation. ZnS is uniformly distributed in the CEI except for the

topmost layer. SO_3^{2-} is mainly distributed in the top and middle regions. The stratified component distribution (SO_3^{2-} @top; ZnF_2 @bottom) constructs a bio-inspired ion highway. SO_3^{2-} -rich top layer attracts Zn^{2+} via electrostatic forces, lowering ion diffusion barrier. While ZnF_2 -rich bottom layer provides electron tunneling paths, it reduces the R_{ct} . Combining the above HRTEM and TOF-SIMS analyses, it could be concluded that the hybrid binder indeed optimizes the spatial distribution of different components in CEI.

To further elucidate the formation mechanism underlying the compositional and spatial disparities in CEI films on NaVO cathode before and after binder modification, theoretical

calculations were conducted to assess the adsorption strength of various polymer molecules on NaVO cathode. As depicted in Figs. 3(a) and 3(b), the calculated adsorption energies of pure PVDF, pure CB, and PVDF-CB hybrid binders on NaVO cathode are -1.59 , -5.89 , and -4.80 eV, respectively. Compared to pure PVDF binder molecule, NaVO cathode shows the enhanced adsorption capacity for the PVDF-CB hybrid binder owing to the fact that each PVDF repeating unit contributes two hydrogen bond donors, while each CB molecular unit provides one hydrogen bond donor and two hydrogen bond acceptors. This also indicates that the introduction of CB could modulate the adsorption strength of PVDF on NaVO, thereby influencing the chemical bond dissociation.

Subsequently, the energy required for C-F and C-O bond

cleavage was calculated for pure PVDF, pure CB, and PVDF-CB hybrid binder polymer molecule on the NaVO cathode. The cleavage energy for C-F bond in pure PVDF adsorbed on NaVO cathode is 0.484 eV (Fig. 3(c)), smaller than that (1.142 eV) for C-O bond in CB molecule (Fig. 3(d)). Notably, the C-F bond is characterized by an even lower cleavage energy, making it highly inclined to rupture preferentially. To be precise, the cleavage energy of the C-F bond drops to 0.169 eV, and in contrast, the cleavage energy of the C-O bond rises to 4.827 eV (Fig. 3(e)), which indicates that ZnF_2 and O-C=O products consequently tend to preferentially form and their proportions will increase. The hybrid binder orchestrates gradient CEI formation through synergistic bond cleavage energetics and molecular interactions. And the extremely low cleavage energy of C-F bond in CB-PVDF

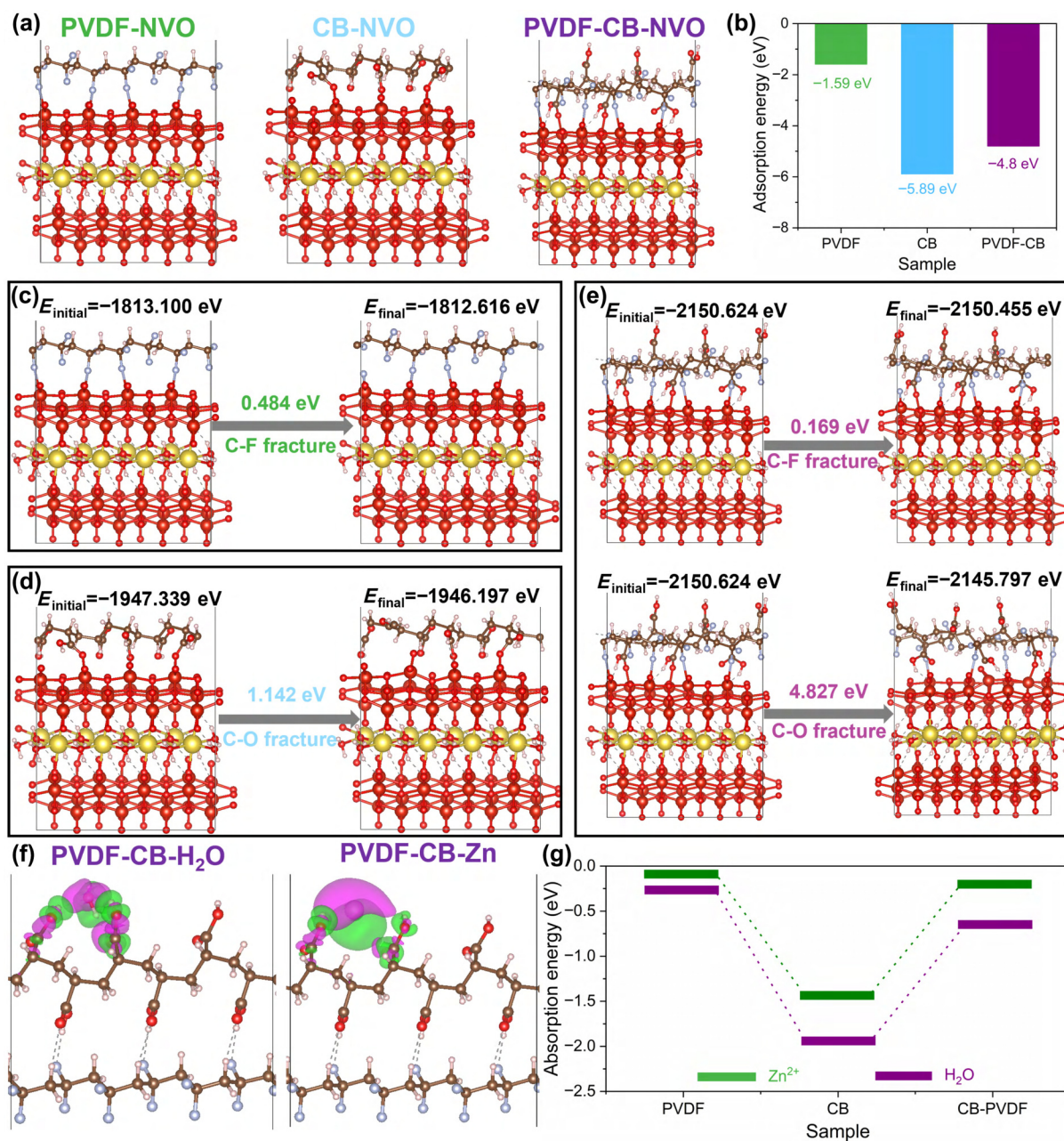


Figure 3 Formation mechanism of gradient CEI. (a) Adsorption configurations of PVDF, CB, and PVDF-CB on NaVO cathode materials. (b) Adsorption energies of PVDF, CB, and PVDF-CB on NaVO cathode materials. (c) Energy required for C-F bond cleavage when using PVDF alone as the binder. (d) Energy required for C-O bond cleavage when using CB alone as the binder. (e) Energy required for C-F and C-O bond cleavage in the PVDF-CB hybrid binder. (f) Charge density difference for H_2O and Zn^{2+} adsorption on PVDF-CB binder. (g) Adsorption energies for H_2O and Zn^{2+} on pure PVDF, pure CB, and CB-PVDF binder, respectively.

hybrid binder (0.169 eV) would dynamically favor the ZnF_2 formation at inner layer via F^- release and reaction with Zn^{2+} . Concurrently, steric constraints of CB and its strong adsorption on cathode (-4.8 eV for CB vs. -1.59 eV for PVDF in Fig. 3(b)) endow it to locate in middle layer, where its carboxyl groups coordinate Zn^{2+} , which facilitates outer ZnO layer growth through hydrolysis on cathode. Kinetic analyses demonstrate the role of hybrid binders in optimizing ion transport. DFT calculations were also employed to evaluate the adsorption energy of Zn^{2+} and H_2O , with the corresponding atomic configurations in Fig. 3(f) on different binders. As illustrated in Fig. 3(g), the hybrid binder reveals a lower adsorption ability for Zn^{2+} and H_2O , compared to pure PVDF, suggesting that it can accelerate the de-solvation effect and inhibit water activity, and thereby facilitate Zn^{2+} transport.

To explore the electrode integrity during cycling process, Fig. 4(a) illustrates morphological evolution of electrodes using PVDF and 20%CB-PVDF binders. The PVDF-based electrode developed cracks during drying process and displayed significant block aggregation after 50 cycles. In contrast, the electrode with 20%CB-PVDF hybrid binder maintained its structural integrity upon cycling, reflecting no cracks or agglomeration. In Fig. 4(b), the diffraction intensity distributions of the (001) and (111) crystal planes exhibit notable inhomogeneity and irregular fluctuations. In stark contrast, the diffraction intensity distributions of the (001) and (111) crystal planes in Fig. 4(c) demonstrate superior reversibility and uniformity. This observation indicates that the

variation in interlayer spacing of the layered structure is confined within a reversible range, with no irreversible structural distortion occurring during Zn^{2+} intercalation/deintercalation. For the (111) crystal plane, the diffraction intensity only presents a slight intensity gradient at the late stage of cycling, which suggests that the ordering of atomic arrangement within the lattice is effectively preserved. To investigate the failure mechanism of batteries with PVDF binders, solid-state ^{19}F Nuclear magnetic resonance (NMR) test was staged for electrodes after 300 cycles. In Fig. 4(d), persistent C-F, Zn-F, and H-F peaks in hybrid binder electrodes indicate the stability of hybrid binder and CEI film, while the absence in electrode using PVDF degradation explains its rapid failure. This notable difference verifies that the hydrogen-bonded network with CB-PVDF improves interfacial cohesion. Regarding vanadium dissolution (Fig. S9 in the ESM), DFT calculations illustrate the adsorption energy of vanadium atom on hybrid binder (-2.51 eV) is significantly more negative than that on PVDF (-0.29 eV) upon CB modulation, indicating superior ion-anchoring capability (Fig. S10(a) in the ESM). The ICP data analysis provides further corroboration that cells utilizing the hybrid binder retained 95.0% of vanadium in cathodes, in contrast to 89.0% with PVDF (Fig. S10(b) in the ESM). Crucially, this inhibition of vanadium dissolution originates from the gradient CEI, which effectively isolates reactive species and reduces electrolyte infiltration.

Thereafter, the bonding variations were detected via *in situ*

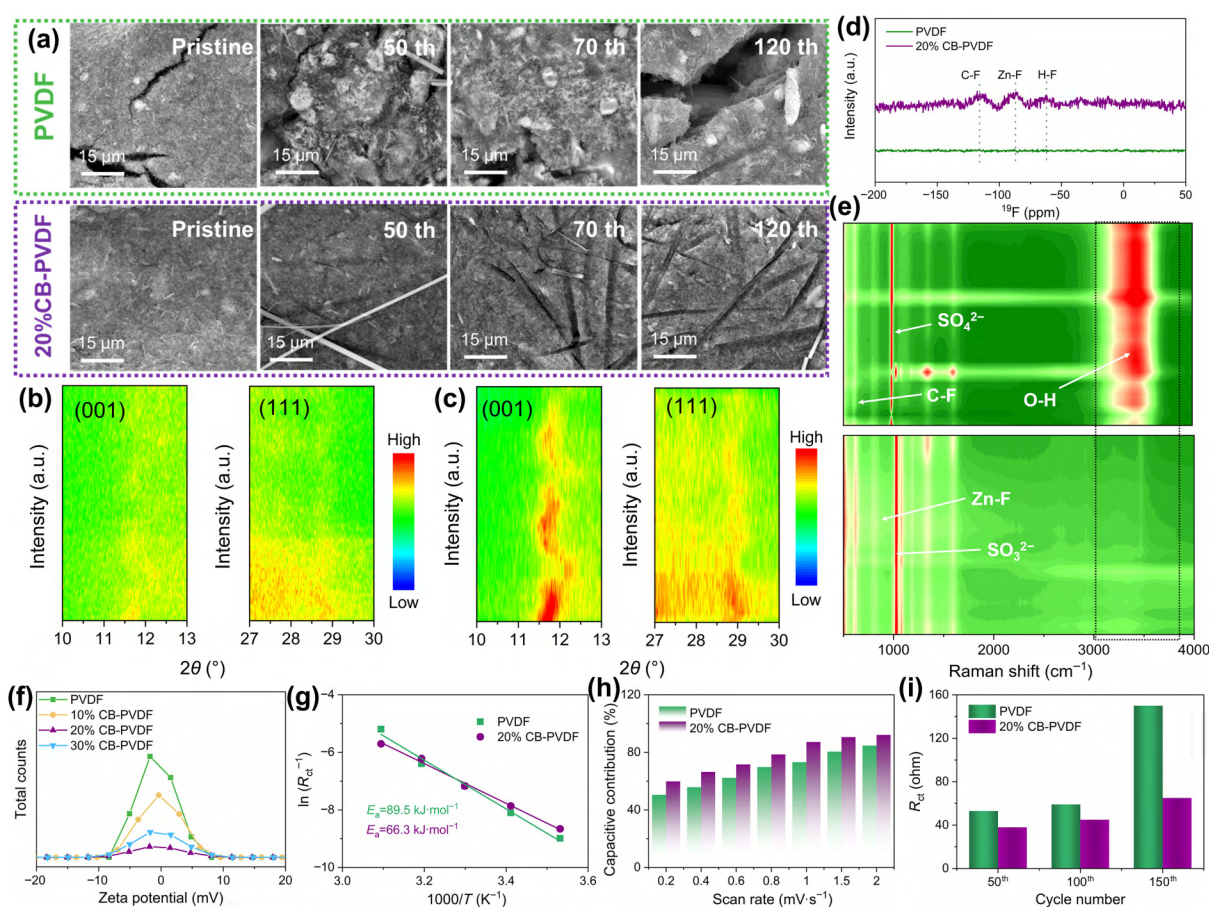


Figure 4 Structural stability and ion diffusion kinetics. (a) Scanning electron microscope (SEM) images of cathodes for cells using PVDF and 20%CB-PVDF after different cycles. (b) Structural evolution of NaVO cathode materials using PVDF binder. (c) Structural evolution of NaVO cathode materials using 20%CB-PVDF binder. (d) ^{19}F NMR spectrum for cycled Zn/NaVO cells using PVDF and 20%CB-PVDF. (e) *In situ* Raman spectrum for the electrodes using various binders. (f) Zeta potentials for electrodes after cycling using different binders to electrolyte. (g) Arrhenius behavior of temperature-dependent reciprocal resistances. (h) Capacitive contributions at various scan rates. (i) Values of R_{ct} after different cycles.

Raman spectra of electrodes using different binders (Fig. 4(e)). The structural stability of hybrid binder was confirmed by the nearly constant C-F bond strength at 850 cm^{-1} . The Zn-F signal peak at 550 cm^{-1} maintains high intensity, ensuring efficient zinc ion transport at cathode/electrolyte interface. Notably, vibrational peaks associated with SO_4^{2-} (980 cm^{-1}) and O-H ($3150\text{--}3500\text{ cm}^{-1}$) indicate the formation of by-products on electrodes using PVDF [42]. In contrast, with the hybrid binder, SO_4^{2-} was replaced by SO_3^{2-} , while the O-H peak intensity significantly decreased, suggesting that the introduction of CB inhibits by-product accumulation on electrode, accelerating zinc ion transfer and alleviating the excessive water molecule accumulation [43]. Further, SEM images after 120 cycles and X-ray diffraction (XRD) patterns after various cycles analyses of electrodes with PVDF and 20%CB-PVDF binders visually confirm suppressed by-product aggregation with 20% CB addition (Figs. S11 and S12 in the ESM). After 120 cycles, the NaVO cathode with pure PVDF exhibits fragmented, agglomerated strips. While the cathode modified with 20%CB-PVDF retains a relatively intact ribbon-like structure at the same magnification (Fig. S13 in the ESM). This indicates that the gradient organic-inorganic hybrid interface formed by 20%CB-PVDF binder on cathode not only inhibits by-product formation but also preserves cathode morphological stability. Therefore, zeta potential analysis was performed with the cycled electrodes with electrolyte, focusing on surface charge density, space charge layer, and ion transport as shown in Fig. 4(f) [44]. The results uncover composition-dependent interfacial characteristics: PVDF electrodes exhibit a nearly neutral potential, yielding poor conductivity despite low ion transport resistance. In contrast, 30%CB-PVDF thickens the space charge layer, hindering Zn^{2+} migration, and 10%CB-PVDF stages particle agglomeration and local polarization. Critically, 20%CB-PVDF enables its potential to confer electrostatic stabilization without excessive space charge, while the continuous PVDF-CB network facilitates concurrent ion transport. This formulation maintains uniform charge distribution, suppresses agglomeration, and balances space charge dynamics-collectively, optimizing electrochemical performance. Subsequently, the Zn//NaVO cells using PVDF and 20%CB-PVDF were assembled to judge its activation energy (E_a) magnitude by EIS plots at different temperatures (Fig. S14 in the ESM) [45]. By linearly fitting $\ln(1/R_{ct})$ versus $1000/T$ in PVDF and 20%CB-PVDF, the slopes could be determined to obtain E_a . Among the tested electrodes, that using 20%CB-PVDF displays a lower E_a value of $66.3\text{ kJ}\cdot\text{mol}^{-1}$, implying the gradient distribution of organic and inorganic components in CEI significantly reduces the energy required for the de-solvation of hydrated zinc ions (Fig. 4(g)). These improvements could be attributed to the stratified CEI structure.

The CV curves at various scan rates for PVDF and 20%CB-PVDF were dissected to explain the capacity contribution mechanism [46]. As the scanning rate increases from 0.2 to $1.0\text{ mV}\cdot\text{s}^{-1}$, the CV profiles for 20%CB-PVDF (Fig. S15(b) in the ESM) retain similar shape and exhibit higher reduction potential than those of PVDF (Fig. S15(a) in the ESM), meaning that derivative active groups facilitate Zn^{2+} intercalation/extraction and mitigate the electrochemical polarization [47]. Furthermore, the b -values could be obtained by fitting redox peak currents and scan rates to estimate the capacity contribution ratios. As demonstrated in Figs. S15(c) and S15(d) in the ESM, the b -values of redox peaks for electrodes range from 0.5 to 1 , indicating that both capacitive and diffusion processes contribute to the capacity of PVDF and 20%CB-PVDF electrodes [48]. At the same scan rate, the electrode

using 20%CB-PVDF reveals a higher diffusion capacity contribution, enabling stable cycling at elevated current density (Fig. 4(h)). Additionally, EIS plots confirm fast charge transfer and ionic diffusion ability [49]. After fitting the curves according to equivalent circuit diagrams (Fig. S16 in the ESM), the charge transfer resistance of electrode using 20%CB-PVDF is smaller than that using PVDF after 50, 100, and 150 cycles, respectively (Fig. 4(i)). This gradient component distribution in CEI enhances diffusion contribution and reduces charge transfer resistance, thereby enabling efficient decoupling of ion and electron transport—a key mechanism for high-rate stability [50].

To evaluate Zn^{2+} storage performance through binder modification, Zn//NaVO cells were assembled using electrodes fabricated with PVDF or 20% CB-PVDF binders, paired with zinc foil anodes, glass fiber separators, and 3 M ZnSO_4 electrolyte. CV scans ranging from 0.4 to 1.6 V were conducted to analyze the voltage polarization upon cycling (Fig. 5(a)) [51]. Evidently, two pairs of observed peaks are related to the redox reactions of $\text{V}^{4+}/\text{V}^{3+}$ and $\text{V}^{5+}/\text{V}^{4+}$ accompanied by (de)intercalation of Zn^{2+} [52]. By comparing the CV curves at $0.2\text{ mV}\cdot\text{s}^{-1}$, the cell using 20%CB-PVDF exhibits a larger specific capacity and smaller conjugate redox peak interval with electrode using pure PVDF, demonstrating a weaker polarization effect, faster reaction kinetics, and higher storage capacity (Fig. 5(b)). As delivered in Fig. 5(c), the self-discharge was measured by charging the cell to a cutoff voltage of 1.6 V and then resting it for 24 h . The 20%CB-PVDF cell shows a smaller voltage drop and higher Coulombic efficiency (CE) compared to that of the pure PVDF cell [53].

Furthermore, the 20%CB-PVDF exhibits superior rate performance (Fig. 5(d)). The cells using PVDF and 20%CB-PVDF were cycled at various current densities of 0.2 , 0.5 , 1 , 3 , 5 , and $10\text{ A}\cdot\text{g}^{-1}$. Reversible discharge capacities for the cell using 20%CB-PVDF could release ~ 437.4 , 378.6 , 326.7 , 276.2 , 223.9 , and $125.7\text{ mAh}\cdot\text{g}^{-1}$, respectively, with significantly higher specific discharge capacity than those of cell using PVDF binder. To further demonstrate the effectiveness of different binders on cycling stability, the cycling performances at $1\text{ A}\cdot\text{g}^{-1}$ are performed in Fig. 5(e). The PVDF cell failed in less than 200 cycles, while the 20%CB-PVDF cell works up to 1000 cycles and still releases a discharge specific capacity of $259.4\text{ mAh}\cdot\text{g}^{-1}$ with a capacity retention rate of 73.3% . As shown in Fig. 5(f), the GCD curve using the PVDF binder exhibits a polarization voltage of 326 mV at the same voltage plateau. However, after introducing CB into PVDF, this polarization voltage is reduced to 278 mV , indicating that CB, as a conductive additive, effectively improves the interfacial ion diffusion kinetics. To verify the efficacy in achieving high-mass-loading AZIBs, the mass loading of NaVO cathode was increased to 5.72 and $7.49\text{ mg}\cdot\text{cm}^{-2}$ to inspect electrochemical cycling performance. Thrillingly, the electrodes using 20% CB-PVDF were cycled without interruption for 2000 cycles with 133.3 and $117.9\text{ mAh}\cdot\text{g}^{-1}$, respectively (Fig. S17 in the ESM). Additionally, the cycling stability with a high mass loading was investigated at $2\text{ A}\cdot\text{g}^{-1}$. The electrode using 20%CB-PVDF delivers a reversible capacity of $143.7\text{ mAh}\cdot\text{g}^{-1}$ after 3000 cycles (Fig. S18 in the ESM).

With a higher current density ($10\text{ A}\cdot\text{g}^{-1}$) (Fig. 5(g)), the cell using pure PVDF as binder fails to operate. PVDF containing 20%CB enables the Zn//NaVO cell to run robustly for 40,000 cycles with a discharge capacity of $52.3\text{ mAh}\cdot\text{g}^{-1}$. It is noteworthy that there is a significant decrease in capacity at initial cycling process, which could be attributed to the participation of zinc ions in the formation process of inorganic/organic hybrid

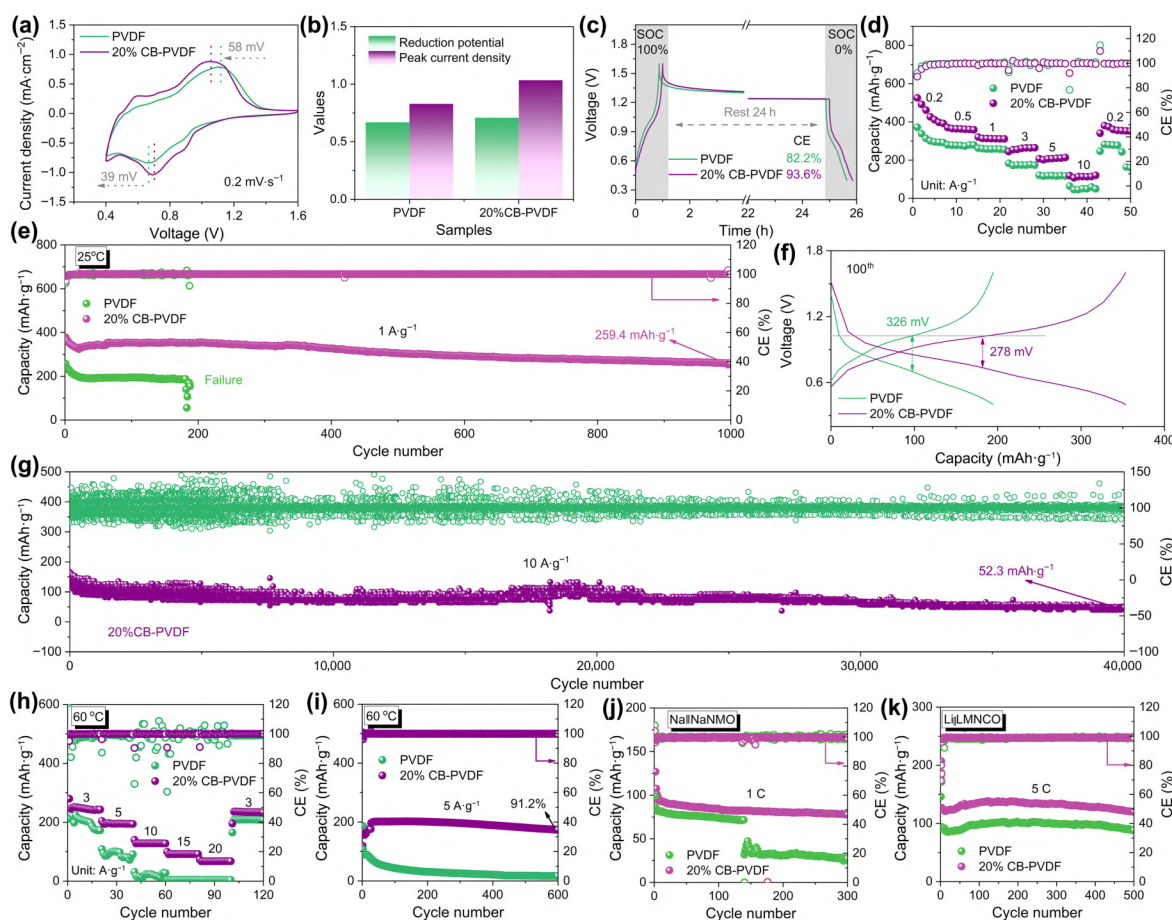


Figure 5 Electrochemical performances and universality. (a) CV curves at $0.2 \text{ mV}\cdot\text{s}^{-1}$ for Zn//NaVO cells using PVDF and 20%CB-PVDF, respectively. (b) Reduction potential and peak current derived from the CV curve. (c) Self-discharge test for Zn//NaVO cells using PVDF and 20%CB-PVDF. (d) Rate performances and (e) cycling performance of $1.0 \text{ A}\cdot\text{g}^{-1}$ at 25°C . (f) The Charge and discharge curves of 100th. (g) Cycling performance at $10 \text{ A}\cdot\text{g}^{-1}$. (h) Rate performances and (i) cycling performances at 60°C . Cycling performances of (j) sodium-ion and (k) lithium-ion batteries.

interface film. In addition, these cells using different binders are also tested at high temperature (60°C) to explore the cathode interface stability as imperatively exacerbated side reactions. Moreover, the rate performances are staged in Fig. 5(h). The 20%CB-PVDF cell releases 248.2, 199.5, 131.2, 97.8 and $72.7 \text{ mAh}\cdot\text{g}^{-1}$ at 3, 5, 10, 15, and $20 \text{ A}\cdot\text{g}^{-1}$, respectively. The cycling performance is tested at $5 \text{ A}\cdot\text{g}^{-1}$. As exhibited in Fig. 5(i), the 20%CB-PVDF hybrid binder endows Zn//NaVO cell with a discharge specific capacity of $188.3 \text{ mAh}\cdot\text{g}^{-1}$ after 600 cycles, which renders a sharp distinction in comparison with that of PVDF cell. Furthermore, the optimized hybrid binder was utilized in sodium-ion and lithium-ion batteries with layered material and lithium-rich manganese-based material (Figs. S19 and S20 in the ESM) as cathode materials to verify universality. Figure 5(j) stages the electrochemical performances of hybrid binder for sodium-ion cells with the $\text{Na}_{0.67}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$ (NaNMO) cathode. The cell using hybrid binder exhibits a capacity retention rate of 90.2% at 1C and could still deliver a discharge specific capacity of $80.3 \text{ mAh}\cdot\text{g}^{-1}$ after 300 cycles. Figure 5(k) interprets the cell for lithium-ion battery using $\text{Li}_{1.2}\text{Mn}_{0.56}\text{Ni}_{0.17}\text{Co}_{0.07}\text{O}_2$ (LMNCO) cathode using hybrid binder could release a discharge specific capacity of $140 \text{ mAh}\cdot\text{g}^{-1}$ after 500 cycles with a capacity retention of 89% at 5C, exhibiting a remarkable efficacy in increasing the specific capacity release, compared to 50% of PVDF. The consistent improvement across different secondary battery systems indicates that regulating the distribution of interfacial film

components guided by hydrogen bonds between binder molecules is a universal interfacial engineering principle.

4 Conclusions

In summary, the carbomer (CB) with a high carboxyl groups content, environmental friendliness, and safety, was deployed as a crosslinker to enhance the functionality of traditional binder in AZIBs via forming stronger intermolecular hydrogen bonding interactions. Specifically, the introduction of CB enhances the intrinsic viscosity of binder, as well as ionic and electrical conductivity. Furthermore, binders containing an appropriate amount of CB enable a gradient distribution of organic and inorganic components in the interfacial film on the surface of cathode materials, thereby improving the charge distribution and transport performance within the interfacial film. Based on the above optimization of the binder and interface, this binder enhances electrode stability and the structural stability of the cathode material, while improving ion diffusion kinetics, thereby achieving a significant enhancement in electrochemical performance. As a result, the hybrid binder endows the Zn//NaVO cells with the ability to achieve 1000 and 40,000 cycles with capacities of 259.4 and $52.3 \text{ mAh}\cdot\text{g}^{-1}$ at 1 A and $10 \text{ A}\cdot\text{g}^{-1}$, respectively. Meanwhile, the hybrid binder enables the electrode to maintain stable cycle for 2000 cycles with 133.3 and $117.9 \text{ mAh}\cdot\text{g}^{-1}$ for bearing mass loading up to 5.72 and $7.49 \text{ mg}\cdot\text{cm}^{-2}$. In addition, this high temperature tolerance is significantly improved due to

the presence of hybrid interfacial films and reactive groups. More importantly, the improved cycling performance for lithium-ion and sodium-ion batteries also demonstrates the broad generalizability of proposed hybrid binder. Therefore, the study addresses the critical issue of electrode instability upon cycling from a binder design perspective, providing a novel approach for designing green, sustainable high-performance secondary rechargeable batteries.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (52072112, 51672069, 12574062, 12204151), Key Project of National Natural Science Foundation of China (92472201), the Zhongyuan Thousand Talents Program of Henan Province (ZYQR201912155), the Henan Overseas Expertise Introduction Center for Discipline Innovation (CXJD2021003), the Program for Innovative Research Team in Science and Technology in the University of Henan Province (20IRTSTHN012), Joint Fund of Science and Technology R&D Program of Henan Province (Young Scientists, 245200810062), the Science and Technology Development Project of Henan Province (202102210105, 192102210235), and the China Scholarship Council (201908090043).

Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

Author contributions

Conceptualization: Shijia Li, Jingwen Zhao, Kai Zhang; Methodology: Shijia Li, Jingwen Zhao, Kai Zhang, Yibing Zhang; Investigation: Jingwen Zhao, Xiaoyan Guo, Zhiyu Song; Visualization: Jingwen Zhao, Peng Lv, Yibing Zhang; Supervision: Peng Lv, Yu Jia, Ying Bai; Writing-original draft: Shijia Li; Writing-review & editing: Peng Lv, Ying Bai.

Electronic Supplementary Material: Supplementary material (optical photographs of the electrodes and binders, resistance values at various locations with the electrodes, XPS spectra, HRTEM images, concentration distribution of different species, atomic adsorption configurations, adsorption energy of different polymer binders for vanadium, XRD patterns, SEM images of electrodes and cathodes, EIS plots, CV curves and cycle performances) is available in the online version of this article at <https://doi.org/10.26599/NRE.2026.9120237>.

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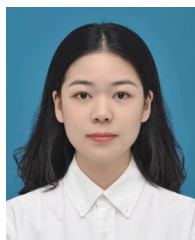
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