

Effects of fluoroethylene carbonate on high-concentration NaClO_4 -based carbonate electrolyte for sodium batteries

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ABSTRACT

Introduction: Anode-free sodium metal batteries have emerged as promising alternatives to lithium-ion batteries (LIBs) due to their high energy density and cost-effectiveness. Nevertheless, their practical implementation is hindered by sodium dendrite growth, an unstable solid electrolyte interphase (SEI), and a limited sodium reservoir, resulting in poor Coulombic efficiency and a short cycle life. High-concentration electrolytes (HCEs) can stabilize Na metal by suppressing solvent-related parasitic reactions and promoting an inorganic-rich SEI, though their high costs and viscosity constitute significant challenges. In this work, an HCE consisting of NaClO_4 in ethylene carbonate (EC)–propylene carbonate (PC) diluted with fluoroethylene carbonate (FEC) is proposed to regulate the solvation structure and induce an anion-derived and F-rich SEI.

Methods: Two HCE formulations with NaClO_4 :EC:PC:FEC molar ratios of 1:2.4:2.4:1 (HELF1) and 1:2.4:2.4:2 (HELF2) were prepared, and a low-concentration electrolyte (1 M NaClO_4 in PC-FEC, 98:2 vol%) was used as the baseline.

Results: Raman spectroscopy revealed that FEC increases the fraction of coordinated Na^+ species and dissociated ClO_4^- . HELF1 and HELF2 exhibit good oxidative stability up to 4.8 V vs. Na^+/Na and improved Na plating/stripping reversibility. However, excessive FEC leads to increased polarization, which is attributed to the formation of a thick, ion-transport-limited, and mechanically fragile SEI. Despite an improvement in the initial Coulombic efficiency (~85%), the Al||NFC full cell retains only 17.2% of its capacity after 25 cycles.

Conclusion: FEC modulates the solvation structure and participates in SEI formation, effectively enhancing the stability of Na metal and the Coulombic efficiency. However, excessive FEC leads to an unstable SEI and poor long-term performance, highlighting the need to optimize its content to balance interfacial stability and ion transport.

Key words: Anode-free sodium batteries, carbonate-based electrolyte, fluoroethylene carbonate, high-concentration electrolytes, sodium perchlorate.

INTRODUCTION

Lithium-ion batteries (LIBs) have been successfully commercialized owing to their high energy density and lightweight nature, enabling their extensive application in portable electronics, power tools, and electric vehicles.^{1,2} However, the growing demand for cost-effective, sustainable, and large-scale energy storage systems has attracted increasing interest in sodium-based rechargeable batteries. Benefiting from the natural abundance and low cost of sodium sources, sodium batteries are regarded as promising alternatives to LIBs while sharing similar electrochemical working principles.³

Sodium metal batteries (SMBs), particularly anode-free sodium batteries (AFSBs), offer a significant advantage in terms of energy density by eliminating excess sodium metal at the anode.^{3,4} Nevertheless, their practical implementation is severely hindered by the

intrinsic instability of sodium metal during repeated sodium plating and stripping. Sodium dendrite formation, large volume fluctuations, continuous electrolyte decomposition, and unstable solid electrolyte interphase (SEI) formation lead to low Coulombic efficiency and rapid capacity decay.^{4,5}

Electrolyte engineering has emerged as an effective strategy to stabilize sodium metal anodes.^{3–7} High-concentration electrolytes (HCEs) can regulate Na^+ solvation structures to form anion-rich solvation shells, resulting in the suppression of parasitic reactions and an enhanced anion-derived SEI. However, they present the drawbacks of high salt consumption and increased viscosity. NaClO_4 features rapid ion transport, good chemical and thermal stability, and low costs, making it attractive for sodium battery research.^{8,9} However, its strong interaction with Na^+ ions and the associated interfacial instability necessitate careful electrolyte design. In addition,

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investigations into carbonate-based HCEs for AFSBs, particularly those employing NaClO_4 salts, remain limited.^{6,10–13} Incorporating film-forming additives into HCEs, typically fluorinated components, offers an effective pathway to regulate electrolyte decomposition and strengthen the interphase. Fluoroethylene carbonate (FEC) has been widely reported to modulate SEI chemistry and sodium deposition in various carbonate- and ether-based electrolytes.^{14–22} According to previous studies, FEC-derived SEI layers are typically compact and stable, leading to more uniform sodium deposition and suppressed dendrite formation.^{15,22} Further, cryo-TEM analyses have revealed that FEC induces the formation of a thin, multilayer SEI; this is typically composed of an amorphous NaF layer over the inner Na_3PO_4 , which effectively inhibits continuous electrolyte reduction.¹⁸ Moreover, the incorporation of FEC in localized HCEs enhances interfacial stability at high voltages via the formation of a robust inorganic-enriched cathode–electrolyte interphase. However, the effect of FEC is strongly concentration-dependent, as excessive FEC may result in mechanically fragile SEI layers with insufficient organic binding components,¹⁴ underscoring the necessity of electrolyte optimization.

In this work, we investigate a NaClO_4 -based HCE using a mixed ethylene carbonate (EC) and propylene carbonate (PC) system, with FEC serving as a diluent and an SEI-forming additive. The influence of the FEC content on the Na^+ solvation structure, sodium plating/stripping behavior, interfacial stability, and electrochemical performance of AFSBs paired with the cathode material is investigated.

MATERIALS AND METHODS

Chemicals

Sodium perchlorate (NaClO_4 , $\geq 98\%$), sodium metal (Na, 99.95%), EC ($\geq 99\%$), PC ($\geq 99\%$), FEC ($\geq 99\%$), *N*-methyl-2-pyrrolidone (NMP, 99.5%), poly(vinylidene fluoride) (PVDF, $M_w \sim 534,000$), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%) were obtained from Sigma-Aldrich. Carbon Super P (C65) was provided by Imerys ($> 99.9\%$), and sodium hydroxide (NaOH , $\geq 98\%$) was supplied by Merck. Iron nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($> 98\%$), and citric acid ($> 99.0\%$) were purchased from Fisher. All chemicals were used as received, without further purification.

Preparation of electrolytes

Electrolytes were prepared by dissolving the desired amount of NaClO_4 in the corresponding solvent systems under continuous stirring for 12 h at room temperature inside an argon-filled glovebox (O_2 and H_2O

< 0.1 ppm). The electrolytes investigated in this work are denoted as follows:

+ ELF-1M: $\text{NaClO}_4/\text{EC}/\text{PC}/\text{FEC}$ (49:49:2, v/v)

+ HEL: $\text{NaClO}_4/\text{EC}/\text{PC}$ (1:2.4:2.4, molar ratio)

+ HELF1: $\text{NaClO}_4/\text{EC}/\text{PC}/\text{FEC}$ (1:2.4:2.4:1, molar ratio)

+ HELF2: $\text{NaClO}_4/\text{EC}/\text{PC}/\text{FEC}$ (1:2.4:2.4:2, molar ratio)

The relatively high FEC contents in the HELF1 and HELF2 electrolytes (corresponding to approximately 16.42 and 28.21% v/v, respectively) were selected to elucidate the effect of FEC on the solvation structure and interfacial behavior of the electrolyte system.

Synthesis of cathode material

$\text{NaFe}_{0.45}\text{Zn}_{0.05}\text{Co}_{0.5}\text{O}_2$ (NFZC) was synthesized via the sol-gel route. Stoichiometric amounts of NaOH , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and citric acid were dissolved in distilled water to form a concentrated precursor solution. Subsequently, a 25% aqueous NH_3 solution was added dropwise to adjust the pH to 3–4. The resulting solution was continuously stirred at 80°C to form a viscous gel. The gel was then preheated at 400°C for 5 h, followed by calcination at 900°C for 12 h in air to obtain the NFZC cathode material.

Electrolyte characterization

Raman spectra were recorded using a Horiba Jobin Yvon Raman spectrometer with an excitation wavelength of 638 nm.

Coin cell assembly and electrochemical measurements

CR2032-type coin cells were assembled in the argon-filled glovebox. Sodium plating/stripping of the $\text{Na}||\text{Na}$ symmetric cells was conducted at a current density of 1.0 mA cm^{-2} with a plating/stripping period of 1 h. Chronoamperometry (CA) measurements for the $\text{Na}||\text{Na}$ cells were performed by applying a constant potential step of 10 mV for 2100 s. $\text{Na}||\text{Al}$ cells were assembled using an Al foil (19 mm in diameter) as the working electrode and a sodium metal foil (15.8 mm in diameter) as the counter and reference electrodes. Sodium deposition in the $\text{Na}||\text{Al}$ cells was capacity controlled at a current density of 1.0 mA cm^{-2} for 1 h, while stripping was voltage controlled with an upper cut off voltage of 1.0 V vs. Na^+/Na . Linear sweep voltammetry (LSV) was performed on the $\text{Na}||\text{Al}$ cells at a scan rate of 0.1 mV

s^{-1} from open-circuit voltage (OCV) to 6.0 V for oxidation and from OCV to -0.5 V for reduction. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a sinusoidal voltage perturbation with an amplitude of 10 mV over a frequency range of 1 MHz to 1 Hz.

Full cells were assembled using HELF1, NFZC, and Al foil as the electrolyte, cathode, and anode, respectively. The NFZC cathode slurry was prepared by mixing 90 wt.% of the active material, 5 wt.% of conductive carbon (C65), and 5 wt.% of the PVDF binder in NMP using a Thinky mixer for 20 min. The homogeneous slurry was then cast onto Al foil and dried under vacuum at 80°C for 12 h. The dried electrode was punched into disks (12.7 mm in diameter) with an NFZC mass loading of $\sim 9\text{--}10\text{ mg cm}^{-2}$ (1 mAh cm^{-2}). A galvanostatic charge–discharge test was conducted at a C/10 rate ($1\text{C} = 150\text{ mAh g}^{-1}$) within the range of 2.0–3.9 V.

LSV, EIS, and CA were carried out on a Biologic VSP-300 potentiostat (France). The sodium plating/stripping and galvanostatic charge–discharge tests were conducted on a LAND CT3002A battery testing system (China). For all cell configurations, 200 μL of the investigated electrolyte was impregnated into two layers of Whatman glass fiber (GF/C) separators.

After cycling, the Al foil electrodes were rinsed with dimethyl carbonate (DMC) and dried under vacuum prior to examining their surface morphology via scanning electron microscopy (SEM, Jeol SM-IT200), operated at an accelerating voltage of 10 kV. The elemental composition was analyzed using an energy-dispersive X-ray spectroscopy (EDS) setup attached to the SEM system.

RESULTS

The physical and electrochemical properties of the low- and high-concentration electrolytes were investigated. **Figure 1a** presents the EIS spectra of the cells, where stainless steel casings and spacers served as the electrodes, separated by two layers of Whatman glass fiber impregnated with the different electrolytes. As expected, the HCEs exhibit higher Ohmic resistance than the baseline ELF-1M due to increased viscosity and enhanced ion pairing and/or ion aggregation, which hinder ion mobility. The ionic conductivity (σ) was calculated according to **Equation 1**:

$$\sigma = \frac{l}{R \times S} \quad (1)$$

where l (cm), R (Ω), and S (cm^2) are the thickness of the two Whatman glass fibers, the Ohmic resistance

(obtained from the EIS measurement), and the circular area of the stainless steel spacer, respectively. The ionic conductivities of HELF1 and HELF2 are lower than that of ELF-1M (**Figure 1b**), consistent with the higher resistance observed in the impedance spectra. The Na^+ transference number indicates the relative contribution of Na^+ ions to the overall ionic conductivity. As illustrated in **Figure 1c**, Na^+ remains the dominant charge carrier in all electrolytes, as reflected by the relatively high Na^+ transference number. A slight decrease in the Na^+ transference number from 0.78 (ELF-1M) to 0.73 (HELF1) can be observed, likely due to the increased formation of ion pairs and/or ion aggregates in a HCE, which moderately impedes Na^+ mobility. Increasing the FEC content in HELF2 notably raises the Na^+ transference number to 0.84, suggesting that FEC acts as a diluent that facilitates the mobility of ion pairs and aggregates. The impedance spectra of the Na||Na symmetric cells before and after the CA test (**Figure 1d**) display semicircles corresponding to the interfacial charge-transfer resistance. Although the ELF-1M electrolyte shows relatively large semicircles, it exhibits a minimal change in its impedance profile; on the other hand, HELF2 exhibits a pronounced growth in the semicircle, which can be attributed to SEI thickening and increased charge-transfer resistance. **Figure 1e** presents the current response during the CA measurements. The HCEs require a longer time to reach a steady state, consistent with their lower ionic conductivity and the increased interfacial impedance. HELF1 exhibits a relatively higher steady-state current, given its high Na^+ concentration and lower charge-transfer resistance.

Figure 1f displays the LSV profiles of Al foil in different electrolytes to exploit their oxidative and reductive stability, with the inset showing enlarged views. During the anodic scan, all electrolytes exhibit oxidative stability up to 4.8 V vs. Na^+/Na . The low-concentration electrolyte shows a larger capacitive current,²³ which can be attributed to the large fraction of solvated ions and solvent molecules participating in interfacial polarization. Interestingly, the low-concentration electrolyte exhibits a slightly higher oxidation onset potential. While FEC-containing electrolytes generally demonstrate improved oxidative stability compared to conventional carbonate electrolytes, theoretical calculations suggest that the oxidation potentials of coordinated species in HCEs can be lower than those of isolated molecules because the oxidation processes are coupled with a high

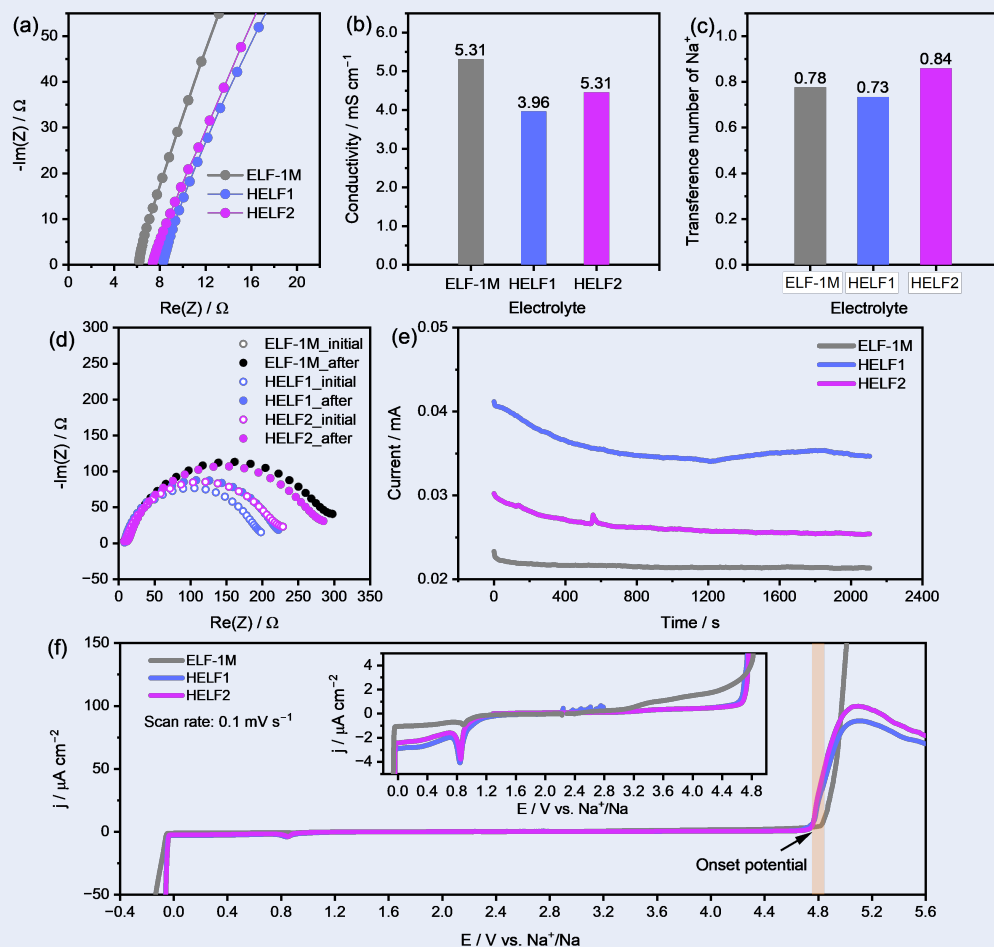


Figure 1: (a) Electrochemical impedance spectra of SS||SS symmetric cells, (b) ionic conductivity, and (c) Na^+ transference number of the electrolytes. (d) Electrochemical impedance spectra of Na||Na cells before and after chronoamperometry, and (e) current response during chronoamperometry. (f) Linear sweep voltammetry (LSV) of Al foil in the different electrolytes. Inset: LSV curves with an adjusted current scale to highlight the weak reduction feature at low potentials. [Source: Authors']

probability of H-transfer reactions.¹⁹ The initial onset of oxidation is likely associated with the oxidation of the ClO_4^- anion, which becomes weakly solvated in the HCEs.²⁴ Subsequent oxidation processes can be ascribed to the formation of EC/PC radical species,^{9,14,24} followed by FEC oxidation at higher potentials. On the cathodic side, a single reduction peak can be observed for all electrolytes; this shifts toward lower potentials with an increasing electrolyte concentration due to the strengthened interactions between Na^+ and solvent molecules. The higher reduction peak at high concentrations indicates a greater tendency of electrolyte reduction. Although the intrinsic electrochemical stability of $NaClO_4$ is lower than that of the carbonate solvents, the observed reduction process is most likely dominated by

FEC reduction, facilitated by the complex interactions among FEC, Na^+ , and EC/PC molecules.²⁰ The sharp increase in current near 0 V corresponds to the deposition of sodium metal on the Al substrate.

The ion-solvent interactions in the electrolytes were elucidated by Raman spectroscopy (Figure 2a). Regarding the low-concentration electrolyte (EL-1M), the band at $720\ cm^{-1}$ is ascribed to the skeletal bending vibration of cyclic carbonate solvents, including PC, EC, and FEC.²⁵ Upon increasing the salt concentration, this band shifts slightly toward higher wave numbers, indicating the coordination of an increased fraction of solvent molecules with Na^+ ions. This shift reflects the enhanced solvent-induced stress exerted by Na^+ on the carbonate ring framework.^{25–27} In addition, in the case of ELF-1M, the C–O stretching vi-

bration of the EC-PC mixture appears at 850 cm^{-1} , while the vibration of PC occurs at 910 cm^{-1} .^{25,28} After introducing FEC, the former band shifts to a higher wave number, and the latter is replaced by a new feature centered at 900 cm^{-1} , suggesting a modified solvent coordination environment around the Na^+ ions.

The asymmetric stretching vibration of ClO_4^- gives rise to two prominent bands in the range of $930\text{--}960\text{ cm}^{-1}$.^{27,29} The band at 930 cm^{-1} is attributed to free solvated ClO_4^- anions, whereas the band near 960 cm^{-1} corresponds to the formation of contact ion pairs or ion aggregates between ClO_4^- and Na^+ .^{30–33} Even in the low-concentration electrolyte, the presence of the high-frequency component indicates the existence of ion pairs, implying non-negligible $\text{Na}^+\text{--ClO}_4^-$ interactions.⁹ With the introduction of FEC into the HCEs, the intensity of the band associated with aggregated ClO_4^- decreases, while the band of free solvated anions increases in intensity. This behavior can be attributed to the partial replacement of ClO_4^- in the Na^+ solvation shell and the effective shielding effect of FEC, arising from its strong interaction with Na^+ . Overall, the transition from ELF-1M to HELF1 and HELF2 is accompanied by significant shifts in the solvent-related peaks, indicating strengthened $\text{Na}^+\text{--solvent}$ interactions in the HCEs, as illustrated in **Figure 2b**. Since FEC exhibits weaker coordination with Na^+ than PC and EC, it preferentially resides in the outer solvation shell. Here, it is more readily exposed at the electrode/electrolyte interface, facilitating electron transfer and, thereby, increasing its susceptibility to electrochemical reduction. Together with the increased population of free ClO_4^- anions, this distinct solvation structure plays a critical role in regulating the formation and composition of the SEI.

Figure 3a displays the effect of electrolyte composition on the stability of the Na||Na symmetric cells. The cells employing HCEs exhibit stable cycling for over 400 h at a current density of 1 mA cm^{-2} , whereas the cell with the baseline fails after 240 h. The voltage fluctuation observed at the end of cycling in the baseline cell can be attributed to unstable SEI evolution, leading to increased interfacial resistance and nonuniform Na plating/stripping behavior.³⁴ This may induce dendritic growth and continuous sodium loss, ultimately leading to cell failure. **Figures 3b–d** present the corresponding DC polarization voltage profiles during sodium stripping/plating over 200 cycles. The baseline shows consistently higher polarization throughout cycling, with a pronounced increase once the stripping or plating capacity exceeds 0.8

mAh cm^{-2} (as indicated by the dashed line). Meanwhile, the cells with HCEs effectively suppress the continuous growth of polarization, even under high-capacity sodium deposition during prolonged cycling. These results indicate that the SEI layers formed in HCEs display greater compactness and ionic conductivity, thereby providing effective interfacial passivation against parasitic electrolyte decomposition and enabling highly reversible plating/stripping. Nevertheless, a gradual increase in the overpotential can still be observed after extended cycling, implying progressive interfacial degradation that ultimately leads to the collapse of cell performance.

Na||Al cells were assembled to further evaluate the reversibility of sodium deposition and the interfacial stability in various electrolytes. As shown in **Figures 4a,b**, the baseline cell exhibits higher polarization (100 mV for ELF-1M compared to 80 mV for HELF1) and a more rapid increase in polarization during sodium plating. Consequently, relatively low first-cycle Coulombic efficiencies of 66.1% and 85.1% are obtained for ELF-1M and HELF1, respectively. **Figure 4c** compares the evolution of the Coulombic efficiency upon cycling. Notably, the influence of the SEI stability and sodium deposition behavior on the cycling performance is significantly amplified in the Na||Al cells compared to the Na||Na symmetric cells, owing to the absence of an excess sodium reservoir. Although the Coulombic efficiency of the ELF-1M cell gradually increases with cycling, it remains consistently lower than that of HELF1, resulting in a shorter cycle life. This behavior indicates that the cell failure in ELF-1M is associated with the formation of an insufficient and unstable SEI, which leads to continuous electrolyte decomposition and progressive thickening of the interfacial layer. Meanwhile, HELF1 facilitates the formation of a partially protective and mechanically stable SEI, mitigating immediate cell failure and suppressing large fluctuations in the Coulombic efficiency during prolonged cycling. These fluctuations possibly originate from repeated SEI fracture/reformation and the concurrent formation and recovery of dead sodium.^{35,36} For comparison, the Na||Al cell using the ELF-1M electrolyte— 1 M NaClO_4 in EC-PC (1:1)—fails to sustain cycling, while a HCE without FEC (HEL, $\text{NaClO}_4\text{:EC:PC} = 1\text{:}2.5\text{:}2.5$) provides low Coulombic efficiency and a short cycle life. Additionally, the HELF2 cell exhibits sodium plating/stripping behavior and SEI characteristics similar to those of the HELF1 cell; however, more significant fluctuations in the Coulombic efficiency can be observed, which ultimately cause cell failure after approximately 40 cycles.

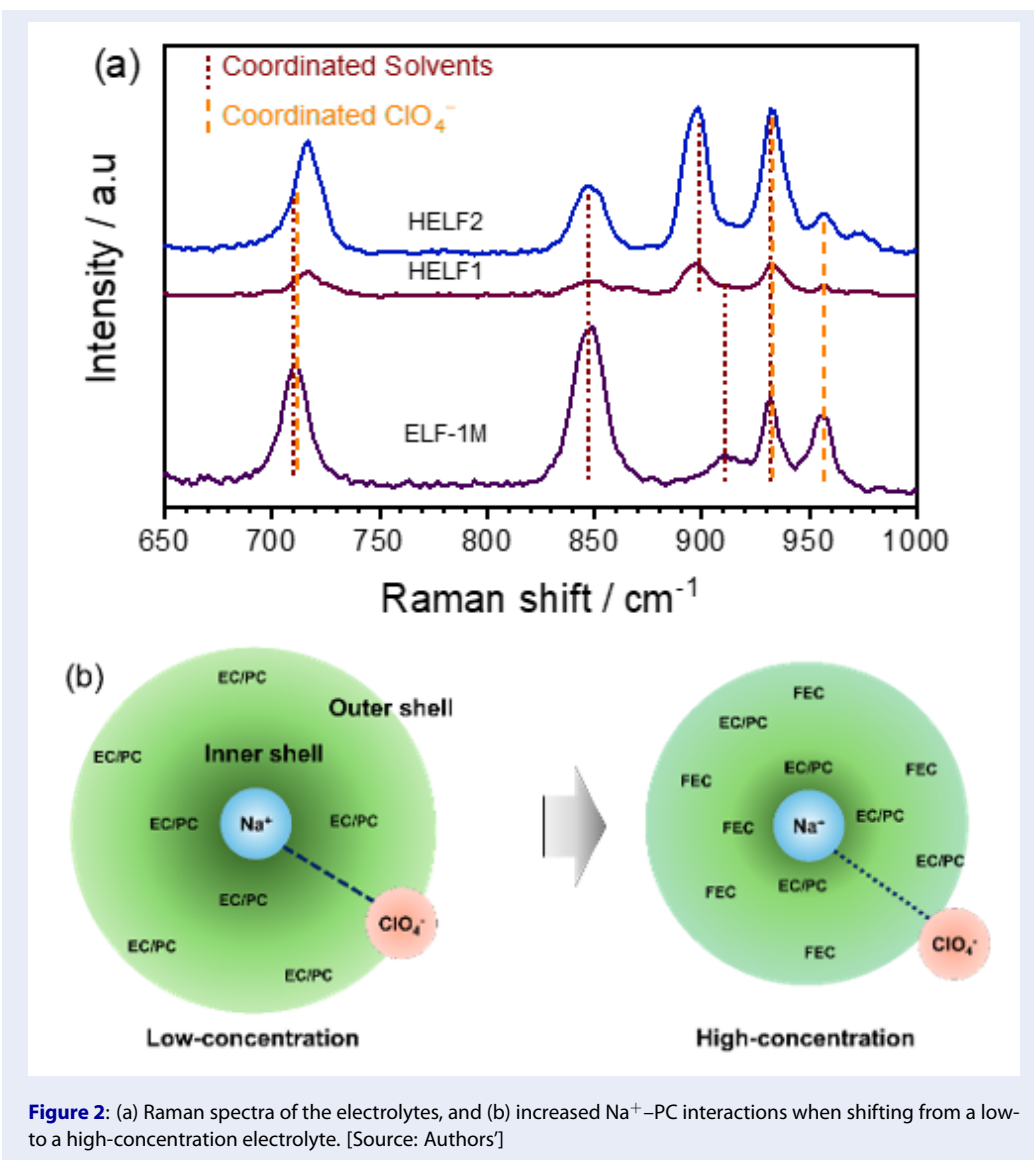


Figure 2: (a) Raman spectra of the electrolytes, and (b) increased Na^+ -PC interactions when shifting from a low- to a high-concentration electrolyte. [Source: Authors']

The sodium deposition morphology on Al foil after 10 plating/stripping cycles in the HCEs is shown in **Figures 5a,b**. The deposited sodium in HELF1 exhibits a relatively uniform distribution across the Al substrate, comprising homogeneously dispersed submicron-sized Na particles; furthermore, no apparent dendrites are observed. Meanwhile, HELF2 produces a smoother and denser surface morphology; this is indicative of the formation of a thicker and more compact interfacial layer, which results from the more extensive participation of FEC and ClO_4^- in SEI formation. Elemental analysis via EDS (**Figures 5c,d**) reveals that the sodium deposits formed in HELF2 contain higher concentrations of F and Cl species and lower contents of O and Na compared

to those in HELF1. These results demonstrate the generation of an SEI enriched in inorganic components, such as NaF and NaCl, derived from the decomposition of FEC and ClO_4^- . Although such an inorganic-dominated SEI is beneficial for early-stage interfacial passivation and contributes to dendrite-free sodium deposition, its increased rigidity and brittleness may be detrimental to long-term mechanical integrity. This feature raises the observed polarization growth and the instability in the Coulombic efficiency in HELF2 during extended cycling.

The full cells performance in the different electrolytes was evaluated. The cell with the low-concentration electrolyte (ELF-1M) delivers an initial specific charge capacity of 145 mAh g^{-1} ; however, only 90 mAh g^{-1}

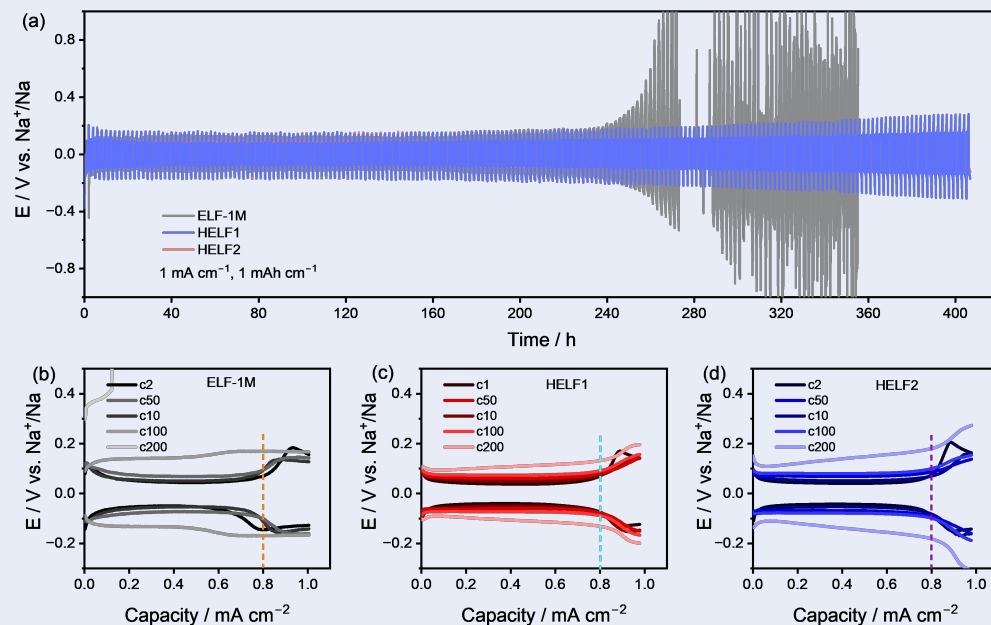


Figure 3: (a) Galvanostatic cycling of Na||Na symmetric cells at a current density of 1 mA cm^{-2} and a capacity of 1 mAh cm^{-2} . Selected voltage profiles for cycling of the Na||Na cells in (b) ELF-1M, (c) HELF1, and (d) HELF2. [Source: Authors']

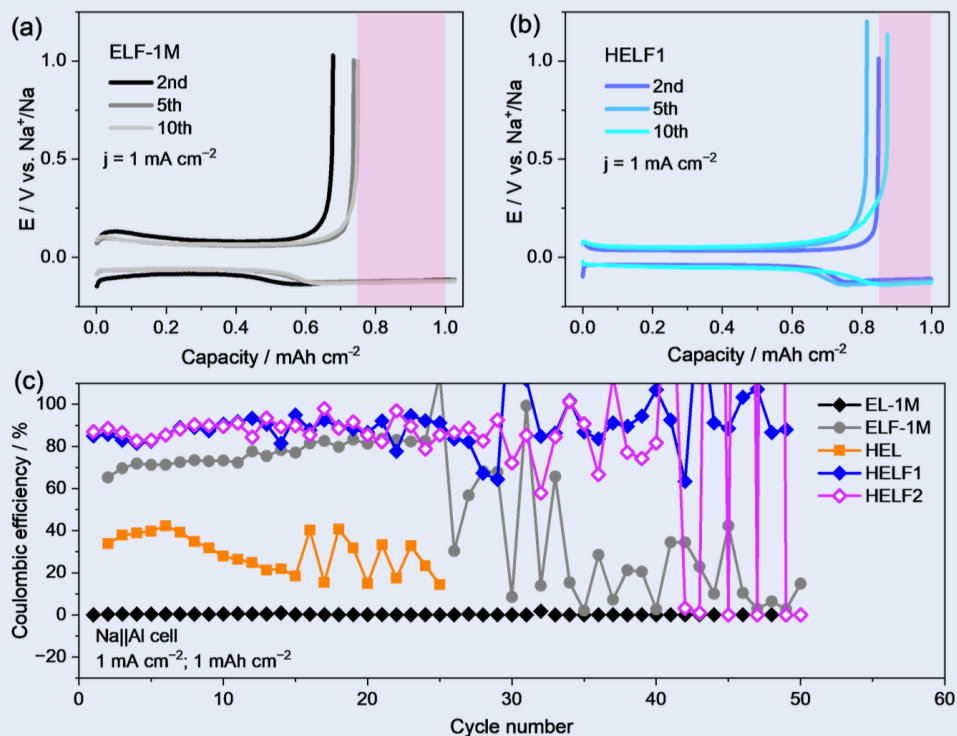


Figure 4: Selected charge–discharge curves during the sodium plating/stripping test of Na||Al cells in the (a) ELF-1M and (b) HELF1 cells, and (c) the corresponding Coulombic efficiency of the cells against the cycle number. [Source: Authors']

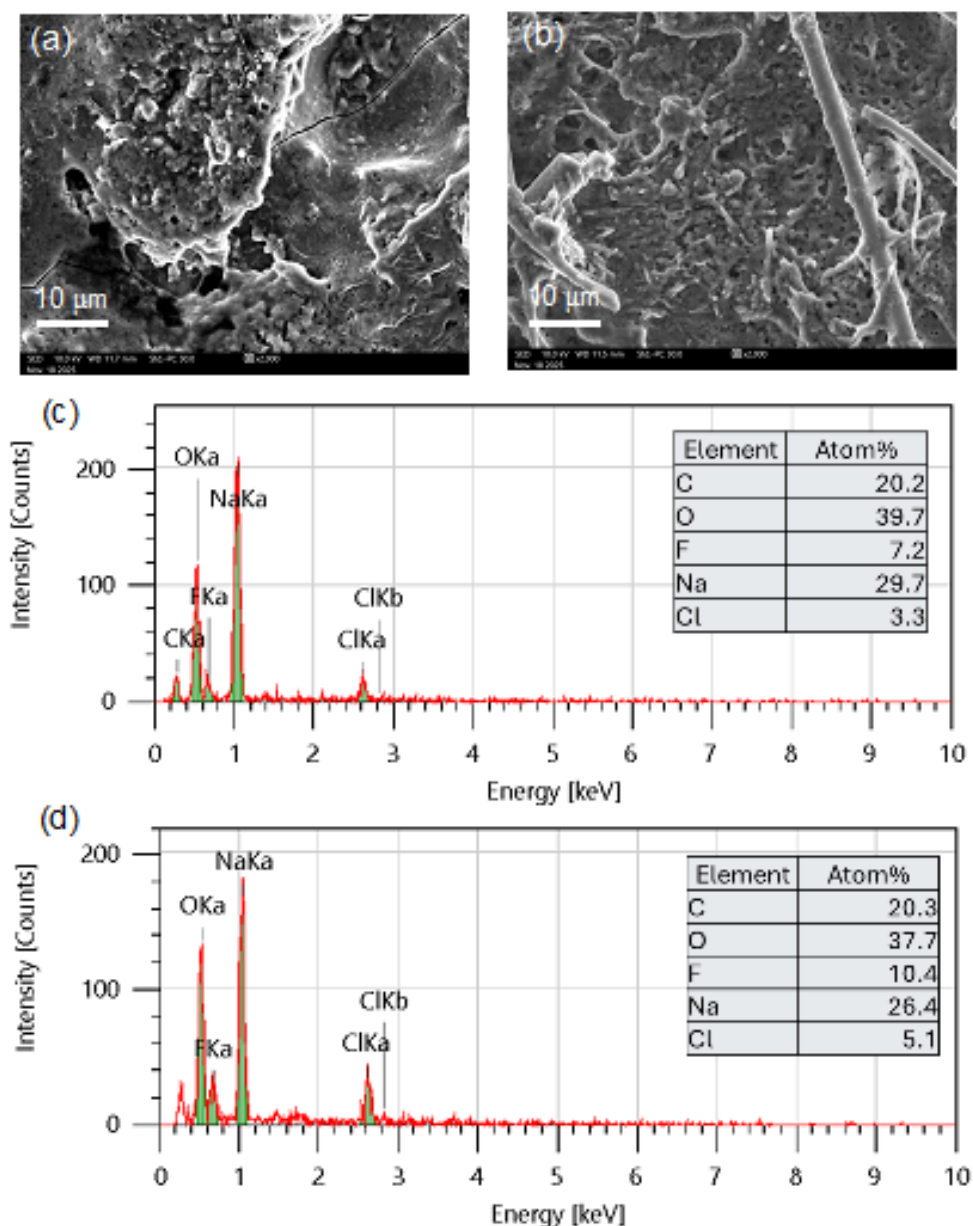


Figure 5: SEM images of sodium deposition on Al foil in (a) HELF1 and (b) HELF2 after 10 cycles at 1 mA cm^{-2} with an area capacity of 1 mAh cm^{-2} and a cut off voltage of $1.0 \text{ V vs. Na}^+/\text{Na}$. Corresponding EDS spectra of the sodium deposits in (c) HELF1 and (d) HELF2 (insets: elemental compositions obtained via EDS analysis). [Source: Authors']

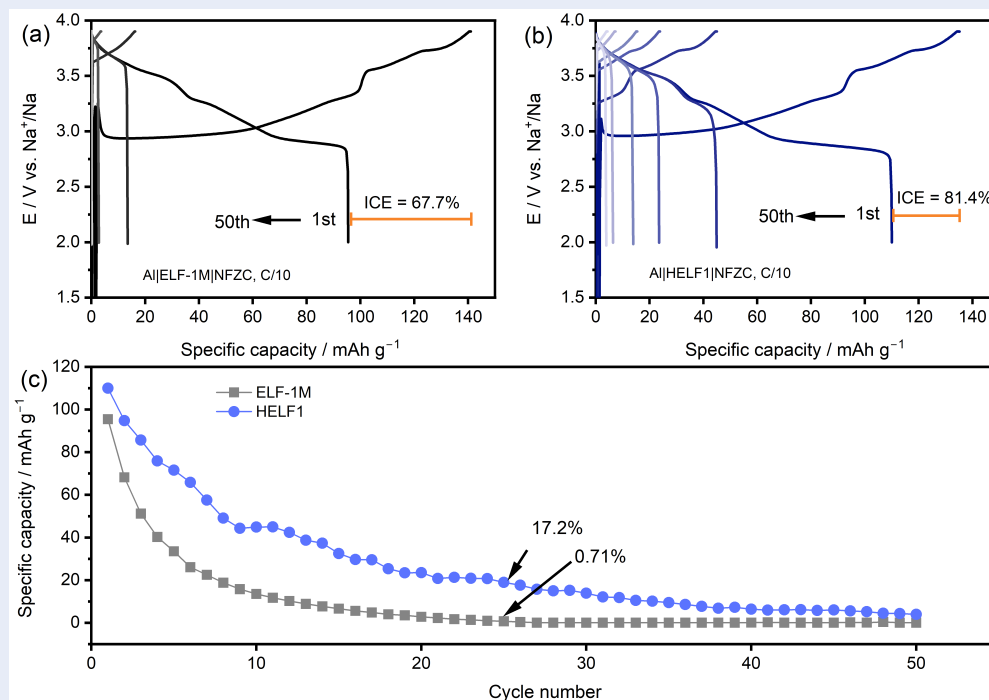


Figure 6: Selected charge–discharge curves of the Al||NFZC cell in (a) ELF-1M and (b) HELF1, and (c) the corresponding capacity as a function of the cycle number. [Source: Authors’]

is recovered during the subsequent discharge, corresponding to a low Coulombic efficiency of 67.7% (**Figure 6a**). In contrast, the cell employing an HCE (HELF1) exhibits a comparable charge capacity while delivering a higher discharge capacity of 110 mAh g^{-1} , resulting in a significantly improved Coulombic efficiency of 81.4% (**Figure 6b**). The cycle life of the anode-free sodium full cells is strongly correlated with their Coulombic efficiency, as the cathode serves as the sole sodium reservoir.^{37,38} As shown in **Figure 6c**, the higher Coulombic efficiency achieved with HELF1, together with the formation of a more protective SEI layer, leads to enhanced capacity retention during prolonged cycling. Specifically, the capacity retention at the 25th cycle reaches 0.71% and 17.2% for the ELF-1M and HELF1 cells, respectively. Nevertheless, all cells ultimately suffer complete capacity depletion after 50 cycles; this is attributed to the continuous sodium inventory loss during repeated cycling, arising from the low Coulombic efficiency of approximately 90% (**Figure 4c**). The sodium loss is mainly attributed to continuous SEI formation and the generation of electrochemically isolated sodium. This observation agrees well with previous studies, where baseline electrolytes with a low Coulombic efficiency also exhibit rapid capacity fading.^{39–42}

DISCUSSION

The use of $NaClO_4$ as the sodium salt in carbonate-based electrolytes, particularly in combination with PC, provides an attractive and cost-effective approach for AFSBs due to its low cost and favorable chemical and thermal stability. However, conventional dilute electrolytes cannot provide reliable AFSB operation. In this work, we investigated whether increasing the electrolyte concentration and introducing FEC can regulate the interfacial chemistry and improve the reversibility of sodium plating/stripping in the $NaClO_4$ –EC–PC system.

In HCEs, stronger Na^+ –solvent interactions significantly alter the solvation environment compared to the low-concentration baseline. At high contents, FEC functions as a cosolvent that modulates the solvation structure²⁰ via weak coordination with Na^+ , partially replacing anions within the Na^+ solvation shell and promoting salt dissociation. This leads to a higher population of free anions while also providing a film-forming additive that directly participates in interfacial decomposition reactions,^{16,22} thereby governing the composition and physicochemical properties of the resulting SEI.

The Na||Na symmetric cells demonstrate that the modified electrolytes enable the formation of rel-

actively compact and ionically conductive SEI layers. These effectively mitigate continuous electrolyte decomposition and reduce interfacial polarization during prolonged sodium plating/stripping, consequently improving cycling stability. However, in practical anode-free cells, such SEI layers cannot ensure long-term cycling durability. The study found that the role of FEC is strongly concentration-dependent. A moderate FEC content enhances interfacial passivation and improves the reversibility of sodium plating/stripping, whereas excessive FEC leads to accelerated performance degradation and a shortened cycle life. Morphological characterizations reveal that sodium deposition becomes smoother and denser with an increasing FEC content. Chemical analyses indicate that the SEI primarily originates from the reduction of ClO_4^- and FEC, resulting in inorganic-rich SEI layers dominated by NaF and NaCl species. While such SEI layers are generally considered chemically robust, they suffer from mechanical fragility. The repeated expansion and contraction of sodium deposits during cycling can cause continuous SEI fracture and reformation, ultimately leading to detachment from the Al foil. Cell failure is likely dominated by aggravated electrolyte decomposition, which is strongly observed at a high deposition capacity; this causes the continuous supply of inorganic species, leading to excessive SEI thickening. At this stage, the sodium deposits evolve to exhibit inhomogeneous and tortuous morphologies that are difficult to fully plate or strip, resulting in the accumulation of electrochemically inactive dead sodium. This complex surface composition and morphology significantly hinder effective ion transport and limit electrochemical accessibility to the Al foil. Notably, the sodium deposits formed in HELF1, characterized by small grain sizes and relatively rough and porous surfaces, provide additional ion transport pathways and accessible deposition sites. This enables more sustained plating/stripping over extended cycles compared to the smoother and denser sodium deposits observed in HELF2. Nevertheless, the uniformly smooth and granular-like sodium deposits are generally favorable for achieving effective protection and ensuring long-term cycling stability. These results indicate that optimization of the sodium morphology alone is insufficient unless electrolyte decomposition is simultaneously suppressed. Therefore, improving the cycling performance in AFSBs requires not only increasing the electrolyte concentration but also preventing persistent electrolyte decomposition via the formation of a robust SEI that simultaneously offers

effective passivation, high ionic conductivity, and sufficient mechanical stability against volume changes during cycling. While the use of FEC is effective in improving the interfacial stability and initial reversibility, the stability of the resulting SEI is insufficient to sustain long-term cycling. Further optimization of the salt concentration and FEC content, together with the introduction of suitable diluents to balance interfacial passivation, ion transport, and mechanical robustness, is essential for realizing highly reversible and stable AFSBs. In this regard, fluorinated ethers can act as effective diluents for constructing thin and protective SEI layers in carbonate- and ether-based electrolytes.^{8,13}

CONCLUSION

In this work, carbonate-based HCEs employing low-cost NaClO_4 were investigated for AFSBs. Increasing the NaClO_4 concentration in combination with a high FEC content effectively regulates the Na^+ -solvent interactions and the solvation structure, promotes extensive salt dissociation, and induces anion-derived SEI formation. FEC also acts as a film-forming additive that participates in interfacial decomposition, facilitating the formation of an inorganic-rich SEI dominated by NaF and NaCl species. Such an SEI provides enhanced interfacial passivation, mitigates continuous electrolyte decomposition, and improves the reversibility of sodium plating/stripping. However, the SEI derived solely from the decomposition of FEC and ClO_4^- is insufficient to guarantee durable sodium plating and stripping on Al foil in anode-free batteries. Therefore, careful optimization of the salt concentration and FEC content, together with the introduction of suitable diluents, is essential to balance interfacial passivation, ion transport, and mechanical robustness and achieve more reversible and stable sodium plating/stripping.

ABBREVIATION

CE: Coulombic efficiency

EC: ethylene carbonate

ELF-1M: electrolyte NaClO_4 1 M/EC-PC:FEC (98:2 v/v)

HELF1: electrolyte NaClO_4 /EC/PC/FEC = 1:2.4:2.4:1, molar ratio

HELF2: electrolyte NaClO_4 /EC/PC/FEC = 1:2.4:2.4:2, molar ratio

FEC: fluoroethylene carbonate

LIBs: lithium-ion batteries

LSV: linear sweep voltammetry

NFZC: $\text{NaFe}_{0.45}\text{Zn}_{0.05}\text{Co}_{0.5}\text{O}_2$

NMP: N-methyl-2-pyrrolidone

OCV: open circuit voltage

PC: propylene carbonate

SIBs: sodium-ion batteries

COMPETING INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR'S CONTRIBUTIONS

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