

Anion-Derived Passivation Interphases for Anti-Corrosion Na Metal and Hard Carbon Hybrid Anode of Sodium Batteries

Yue Li ^a, Minfei Fei ^{a,b,c}, Haiming Wang ^{a,b}, Jianwei Hu ^{a,b}, Huajie Zhang ^{a,b}, Shujuan Han ^{a,b}, Jingyi Xiao ^a, Xin Wang ^a, Xujie Cheng ^a, Manish Chhowalla ^c, Jia Zhu ^{a,b}, Yan Jin ^{a*}

[a] National Laboratory of Solid State Microstructures, School of Sustainable Energy and Resources, School of Advanced Manufacturing Engineering, Frontiers Science Center for Critical Earth Material Cycling, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Suzhou, 215163, P. R. China

[b] College of Engineering and Applied Sciences, Jiangsu Key Laboratory of Artificial Functional Materials, Nanjing University, Nanjing, 210093, P. R. China

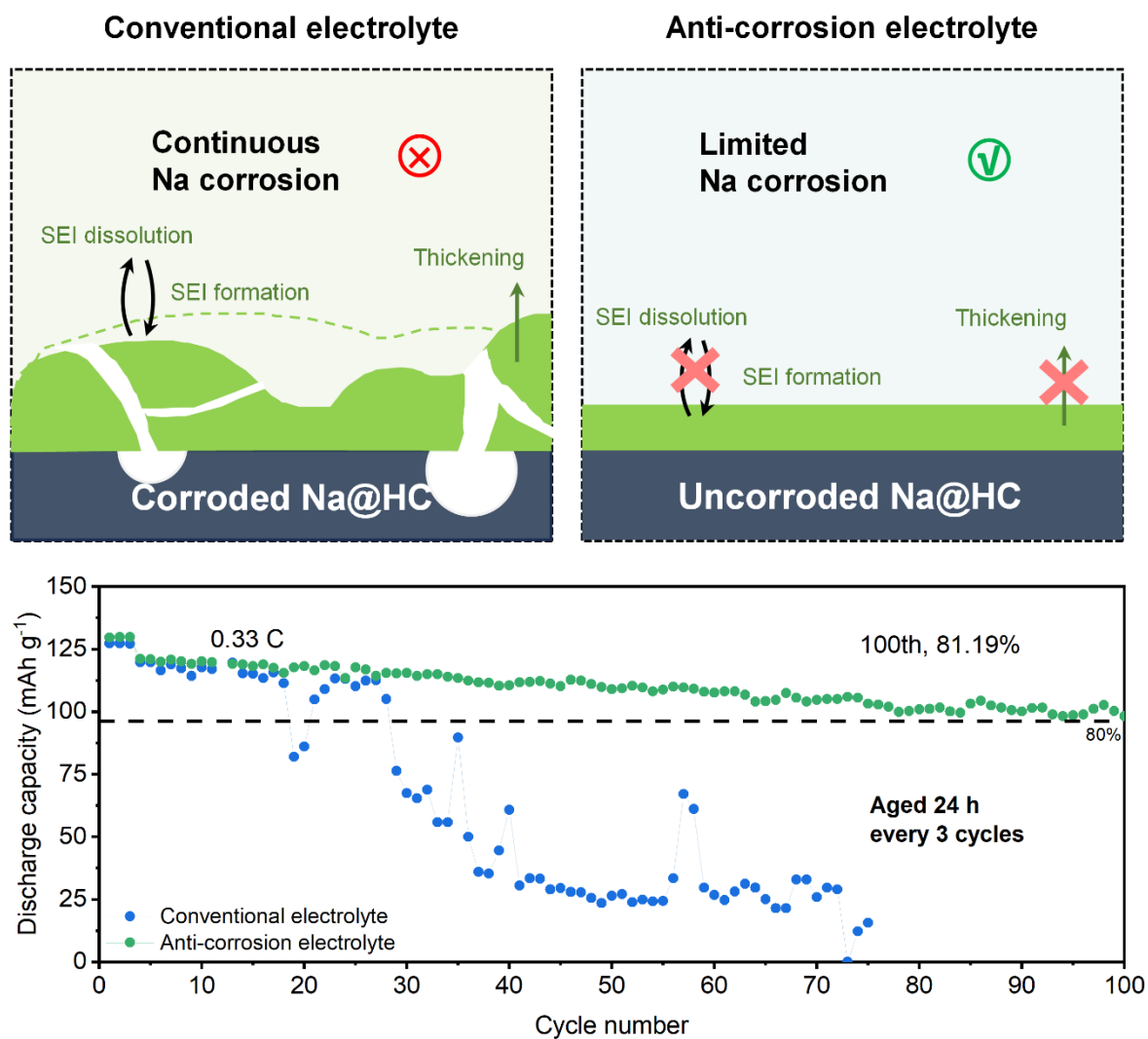
[c] Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, CB3 0FS, United Kingdom

* E-mail: yanjin@nju.edu.cn

ABSTRACT

Sodium batteries hold great promises for energy storage due to material abundance, yet fall short in energy density. Hybrid anodes integrating sodium metal and hard carbon (HC) boost energy density yet face poor aging stability. Herein, we report a NaFSI/1,2-dimethoxyethane (DME)-1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE) electrolyte, which enhances both anode and cathode interfacial stability via anion-derived interphases, mitigating hybrid anode corrosion and preserving cathode structural integrity during high voltage cycling. Consequently, the full cell with a high loading cathode (1.68 mAh cm^{-2}) and limited Na inventory ($\text{N/P} = 1.91$) achieves 87.98% capacity retention after 200 cycles at 0.33 C and 99.82% average Coulombic efficiency. Notably, under intermittent cycling (24 h rest every 3 cycles), it retains 81.19% capacity after 100 cycles, outperforming conventional electrolytes that fail at ~ 75 cycles. This study proposes an anti-corrosion electrolyte to realize hybrid sodium batteries with superior cycling longevity, providing insights into high energy density metal/ion batteries.

TOC Graphics



Sodium-ion batteries (SIBs) are promising candidates for next generation energy storage systems due to the material abundance.¹⁻⁴ However, state-of-the-art SIBs typically demonstrate a moderate energy density around 150 Wh kg⁻¹, as a result of the rather limited specific capacity of conventional electrodes (e.g., 300 mAh g⁻¹ for HC anode).^{1,5} Metallic sodium anode, with a theoretical specific capacity of 1165 mAh g⁻¹, offers a promising approach towards higher energy density, particularly at a high Na metal utilization rate (i.e., a low negative to positive electrode capacity ratio, N/P < 2).^{6,7} However, the cycling stability of low N/P ratio Na metal batteries remains challenges because of severe side reactions, such as Na dendrite growth, dead Na formation and Na corrosion. To this end, hybrid anode integrating HC with metallic sodium has been proposed, to enhance the energy density while balancing interfacial side reactions through strong Na-HC interactions for improved cycling stability.^{8,9}

Nevertheless, in practical application, the overall performance of the hybrid Na batteries, which deploy the hybrid Na-HC anodes, is primarily determined by both cycling stability and calendar aging stability, with the latter remains poorly explored. During calendar aging, corrosion of the hybrid anode is often of decisive significance towards fast capacity loss, and subsequently, fast cell failure. Specifically, metallic sodium tends to evolve into the much less electrochemically active state of sodium containing compounds upon contact with surrounding electrolytes, concurrently accompanied by continuous electrolyte reduction and solid-electrolyte interphase (SEI) thickening.¹⁰⁻¹³ Ideally, this SEI layer should act as a dense and electronically insulating barrier that prevents further parasitic reactions while maintaining sufficient ionic conductivity for Na⁺ transport.¹⁴ However, in practice, the SEI formed in conventional electrolytes is often chemically unstable and mechanically fragile, leading to repeated SEI rupture and regeneration.

This results in deteriorated interphase protection against electron leakage during long-term battery storage, which further accelerates Na inventory loss, accompanied by fast electrolyte depletion and buildup of interfacial impedance.¹⁵ Therefore, stabilizing the Na/electrolyte interface and mitigating corrosion of the hybrid anode are essential prerequisites for extending the calendar life and ensuring the practical application of hybrid sodium batteries.

Here we report an anti-corrosion electrolyte (NaFSI/DME-TTE, molar ratio: 1:1.2:0.8) to address the parasitic corrosion challenge in hybrid sodium batteries. This electrolyte establishes an anion-derived SEI with strong passivation ability to minimize Na corrosion, and enhances cathode structure stability by suppressing transition metal (TM) dissolution and crack propagation. Therefore, the average Coulombic efficiency (CE) loss of the hybrid anode (denotes Na@HC) during 24 h aging was suppressed by approximately 4.35 times, compared to the baseline electrolyte (1 M NaPF₆/1,2-dimethoxyethane, denotes NaPF₆/DME). This enables a stable hybrid sodium battery with 81.19% capacity retention after 100 cycles under harsh aging protocol (with 24 h aging every three cycles), while the cell quickly fails after ~75 cycles with the baseline electrolyte NaPF₆/DME. Overall, this anti-corrosion electrolyte significantly extends hybrid Na battery longevity with 87.98% capacity retention over 200 cycles, achieved with high cathode loading (1.68 mAh cm⁻²) and limited Na inventory (N/P = 1.91). This work assesses calendar aging performance of hybrid Na anodes, and provides valuable insights into electrolyte designs towards high energy density sodium-based batteries.

Anti-corrosion electrolyte design for hybrid sodium batteries

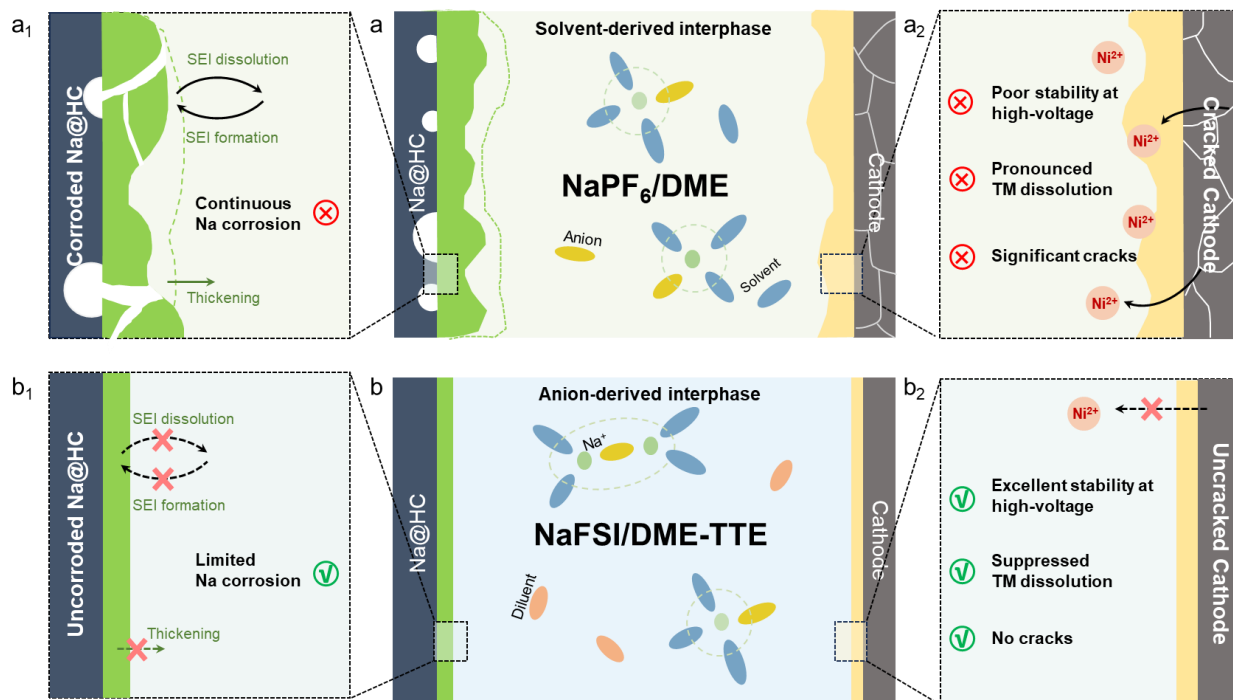


Figure 1. Electrolyte design to enhance interphase stability in hybrid sodium batteries. Schematic illustration of Na corrosion and cathode degradation in full cells with (a) NaPF₆/DME and (b) NaFSI/DME-TTE electrolytes.

Achieving high energy density in hybrid sodium batteries requires a low N/P ratio and high voltage.^{9,16} The widely reported baseline electrolyte NaPF₆/DME, although generally regarded as Na metal compatible, can facilitate the formation of solvent-derived SEI, which is chemically unstable, fragile and partially soluble. This SEI cannot effectively passivate the hybrid anode (Na@HC), leading to continuous Na corrosion (Fig. 1a₁), which is particularly detrimental under low N/P ratio. Therefore, to effectively suppress corrosion of the hybrid anode, electrolyte and SEI should satisfy the following criteria. First, the electrolyte should provide a strong barrier against reduction, thereby preventing SEI overgrowth.¹⁷ Second, the SEI must exhibit excellent electronic insulation to block electron transfer pathway between the electrolyte and Na metal to mitigate Na corrosion.^{10,18,19} Third, since Na-based SEI is reported to be more soluble than its Li counterpart

by one order of magnitude, minimizing its solubility by forming an anion-derived SEI is equally crucial to maintaining long-term SEI integrity.²⁰⁻²⁴ In summary, designing an advanced reduction-stable electrolyte that can construct an anion-derived SEI with high passivation and low solubility fulfills the above criterias and therefore is a promising strategy for enhancing the anti-corrosion capability of hybrid Na anodes.

Spontaneously, maintaining cathode structural integrity during high voltage cycling also presents a major obstacle (Fig. 1a₂). Due to the relatively high highest occupied molecular orbital (HOMO) energy level of DME, the baseline electrolyte NaPF₆/DME undergoes severe oxidative decomposition below 4 V, resulting in the formation of a solvent-derived cathode-electrolyte interphase (CEI).^{25,26} This unstable CEI fails to effectively suppress TM dissolution, which induces irreversible phase transitions and accelerates capacity fading. Besides, the consequent anisotropic stress promotes the propagation of cracks within the cathode, continuously exposing fresh active surfaces to the electrolyte and further aggravating TM dissolution and active material loss.^{27,28} Therefore, constructing a compact and robust CEI is crucial for preserving the structural integrity of high voltage cathodes.

To overcome these interfacial challenges, we designed an anti-corrosion NaFSI/DME-TTE electrolyte capable of simultaneously stabilizing both anode and cathode interphases (Fig. 1b₁-b₂). The FSI⁻ anions participate directly in interphase formation, yielding an insoluble, inorganic-dominated SEI that effectively inhibits sodium corrosion. Meanwhile, on the cathode side, a dense, anion-derived CEI with high oxidation resistance and strong mechanical integrity can mitigate TM

dissolution and crack propagation under high voltage operation. Consequently, the NaFSI/DME-TTE electrolyte concurrently achieves passivation at both electrodes, providing a viable pathway toward hybrid sodium batteries with enhanced energy density, long cycle life, and excellent calendar aging stability.

Electrochemical stability of Na@HC hybrid anode

The corrosion performance and reversibility of Na@HC hybrid anode in the two electrolytes were quantitatively analyzed. The corrosion behavior of deposited Na was quantified by measuring the loss of CE (Δ CE) at varying aging times. In half cells, as shown in Fig. 2a, after the first, fourth, and eighth 24 h aging periods, the average Δ CE of the NaFSI/DME-TTE electrolyte was 0.10, 0.15, and 0.05%, respectively, compared to 0.27, 0.87, 1.11% in the NaPF₆/DME electrolyte, indicating that the designed electrolyte effectively mitigates continuous corrosion of the hybrid anode. We further evaluated calendar aging performance in Na@HC||NaMn_{0.33}Fe_{0.33}Ni_{0.33}O₂ (NaMFN) full cells by resting for 24 h every three cycles during long-cycling (Fig. S1)¹¹, where Na inventory is limited (N/P = 1.91). As depicted in Fig. 2b, Δ CE of the full cell in two electrolytes also showed obvious differences. After the first, second, fourth, and sixth 24 h aging periods, the Δ CE of the NaFSI/DME-TTE electrolyte was 2.07, 1.68, 0.23, and 0.06%, respectively, compared to 2.61, 2, 2.05, 2.84% in the NaPF₆/DME electrolyte. This led to huge differences in the capacity retention during long cycling with 24 h rest every three cycles, where NaFSI/DME-TTE electrolyte retained 81.19% capacity after 100 cycles (Fig. 2c). In contrast, the capacity of the NaPF₆/DME electrolyte degraded precipitously after a short cycling period, eventually losing all reversible Na inventory after approximately 75 cycles. This observation further supports the conclusion that corrosion is a primary cause of capacity loss in hybrid sodium batteries.

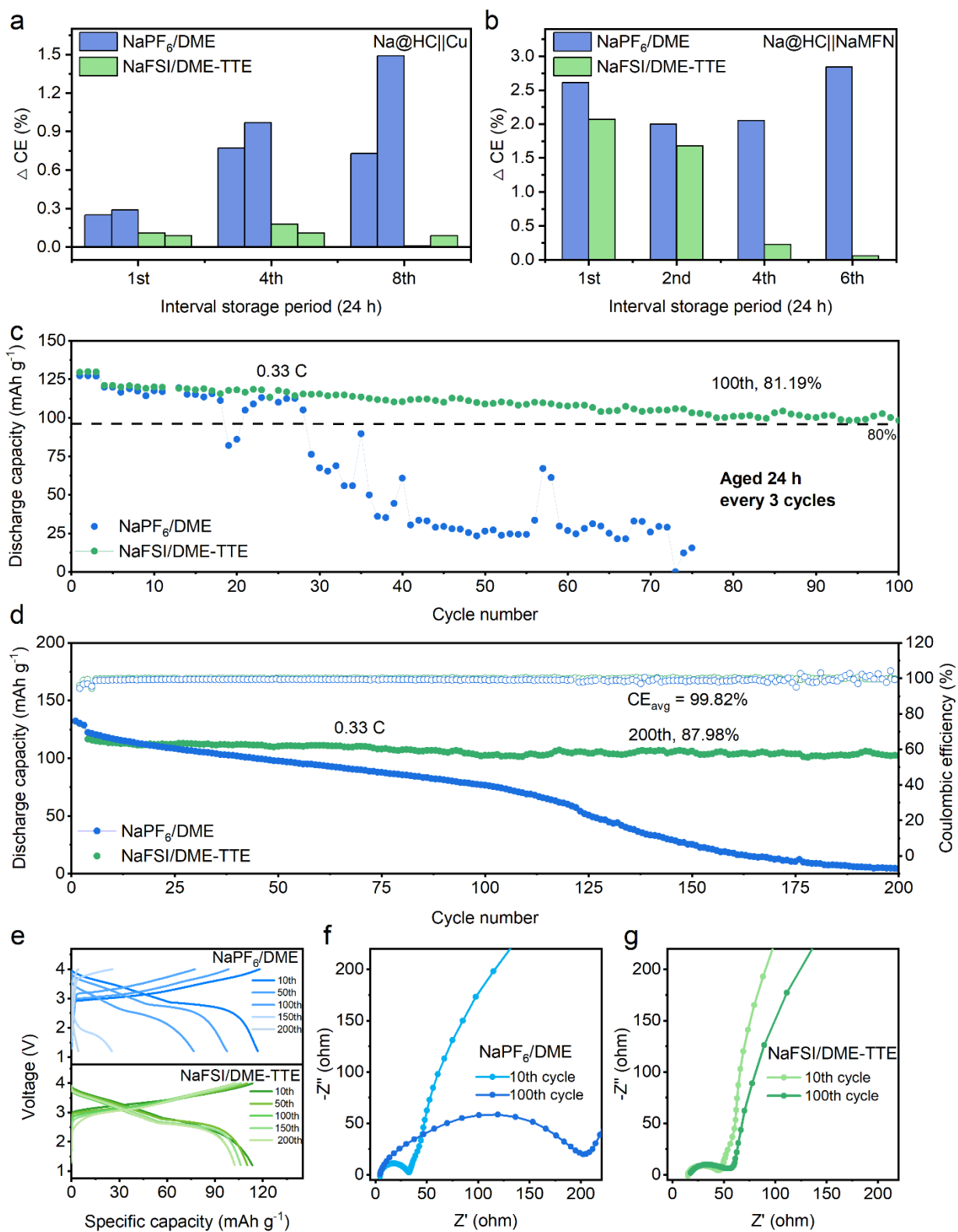


Figure 2. Electrochemical behaviors of half cells and full cells in two electrolytes: (a) Δ CE of hybrid anode in Na@HC||Cu half cell with 24 h calendar aging every three cycles; (b, c) Δ CE and discharge capacity of Na@HC||NaMFN full cells with calendar aging every three cycles; (d) Long-cycling performance of Na@HC||NaMFN full cells at 0.33 C after three formation cycles at 0.1 C; (e) Voltage profiles as a function of cycle number using two electrolytes; (f, g) Ex-situ electrochemical impedance spectra curves of two electrolytes at a fully discharged state.

The reversibility of hybrid anode was subsequently compared. As shown in the Fig. S2, the CE steadily improved and stabilized over 99% in the NaFSI/DME-TTE electrolyte, indicating enhanced reversibility of sodium metal which contribute to the long-cycling stability of the hybrid sodium batteries. When the N/P ratio of full cell is close to 2, the designed NaFSI/DME-TTE electrolyte shows much better stability than baseline NaPF₆/DME electrolyte, with 87.98% capacity retention and 99.82% average coulombic efficiency (CE_{avg}) after 200 cycles at 0.33 C. In contrast, the full cell employing NaPF₆/DME electrolyte shows continuous capacity decay, with 3.59% capacity retention for 200 cycles and 99.1% average CE (Fig. 2d). Moreover, the voltage hysteresis gradually increases in NaPF₆/DME electrolyte, accompanied by severe capacity decay.⁶ In contrast, the NaFSI/DME-TTE electrolyte exhibited no obvious voltage hysteresis as the cycling progressed, and the capacity remained stable (Fig. 2e). The huge difference in the corrosion and reversibility of two electrolytes was further confirmed by impedance (Fig. 2f and Fig. 2g). At the 10th cycle, there is no significant difference in charge transfer resistance (R_{ct}) in two electrolytes. However, after 100 cycles, the R_{ct} in NaPF₆/DME electrolyte increases dramatically, while there is no obvious change in NaFSI/DME-TTE electrolyte. This further confirm the capacity degradation is originated from the drastic change of interphase.²⁹

Characterization of anti-corrosion hybrid anode

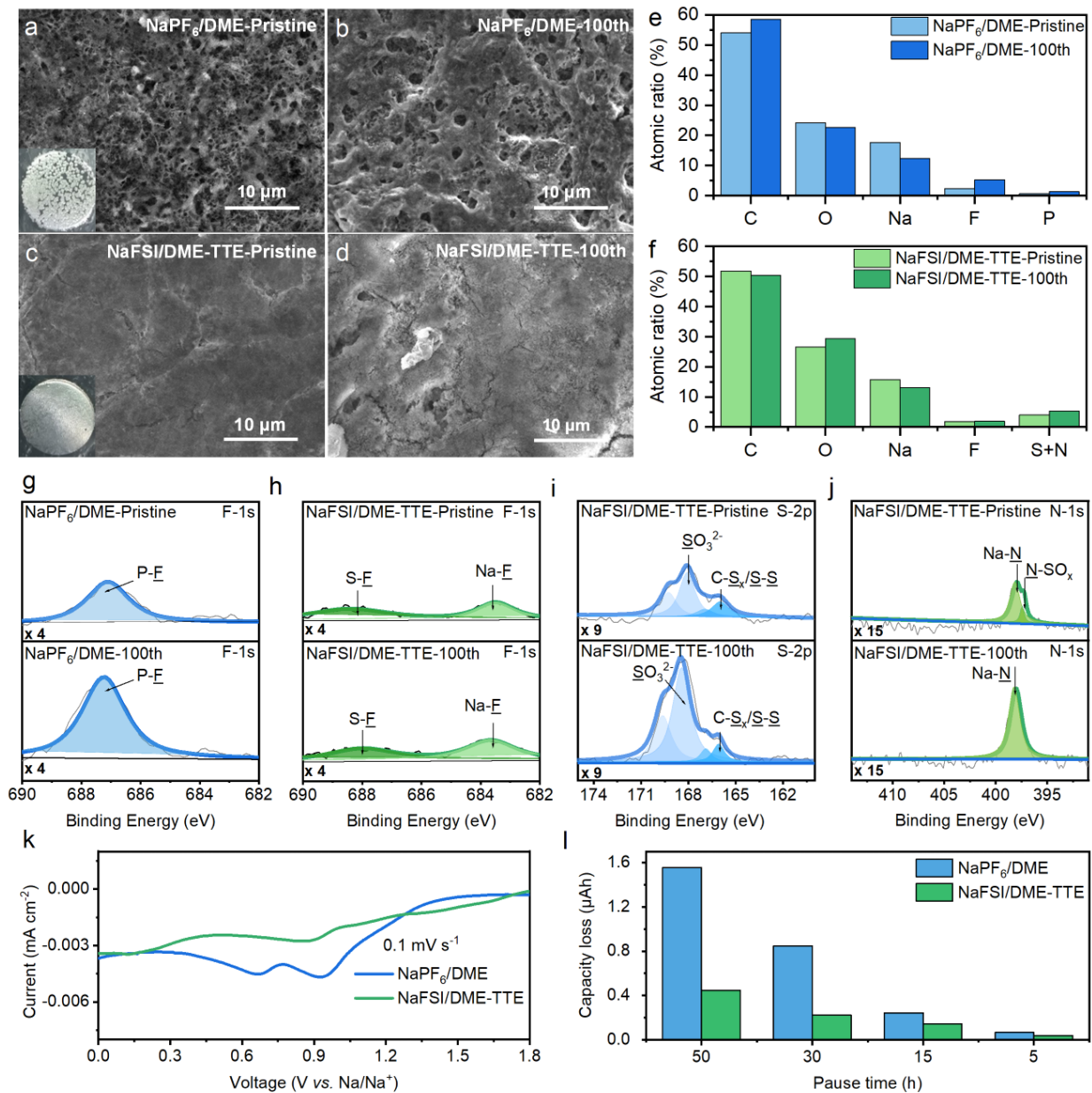


Figure 3. Characterizations of the hybrid anode interface in two electrolytes: (a, c) SEM images of the pristine hybrid anodes prepared in (a) NaPF₆/DME and (c) NaFSI/DME-TTE electrolytes; (b, d) Morphology of the hybrid anodes at the Na deposition state after 100 cycles in (b) NaPF₆/DME and (d) NaFSI/DME-TTE electrolytes; (e-f) Atomic ratio of SEI generated in two

electrolytes for different stages; (g-j) the XPS spectra of hybrid anodes cycled in two electrolytes; (k) The reduction potential of two electrolytes; (l) The capacity loss for different pause times in two electrolytes, where each bar represents the average value of two cells.

Corrosion causes obvious change in the morphology and interphase properties of the hybrid anode. The pristine hybrid anode achieved in the baseline electrolyte NaPF₆/DME was porous and inhomogeneous (Fig. 3a), while the anti-corrosion electrolyte NaFSI/DME-TTE led to compact and dense Na deposition morphology (Fig. 3c). This was originated from initial SEI differences, where NaFSI/DME-TTE formed a more uniform and denser SEI, which not only inhibits Na corrosion but also promotes the subsequent uniform deposition of sodium metal.³⁰ Consequently, Na@HC hybrid anode remains its original flat and smooth morphology in NaFSI/DME-TTE after 100 cycles. The porous Na metal and the larger surface area of hybrid anode in NaPF₆/DME electrolyte accounted for severe Na corrosion and thus low reversibility and CE (Fig. 3b and Fig. 3d).

We conducted X-ray photoelectron spectroscopy (XPS) for a full examination of SEI components on the hybrid anodes in both electrolytes, at pristine state and after 100 cycles (Figs. 3e-f). Notably, the inorganic elements in the NaFSI/DME-TTE electrolyte (5.84% for F, S, and N species) were almost double of those in the NaPF₆/DME baseline electrolyte (2.92% for F and P species). High resolution XPS spectra (Figs. 3g-j, Figs. S3-S4) further verify the formation of anion-derived inorganic-rich SEI components. The F-1s signal in NaPF₆/DME shows a pronounced increase after 100 cycles (Fig. 3g), confirming extensive electrolyte decomposition associated with corrosion. In contrast, in the NaFSI/DME-TTE electrolyte, strong F, S, and N signals are observed both at the

pristine state and after 100 cycles,³¹⁻³³ reflecting stable formation of FSI⁻-derived inorganic species (Figs. 3h-j). In contrast, the SEI layer in the NaFSI/DME-TTE electrolyte contains a higher concentration of NaF compared to the NaPF₆/DME electrolyte, which can inhibit Na corrosion because of NaF with the largest bandgap ($E_g = 6.095$ eV), enhances the electronic insulating properties of the SEI.³⁴ Additionally, NaF's high lowest unoccupied molecular orbital (LUMO) energy level results in weak electron affinities, which indicates the low electron driving force between the hybrid anode and electrolyte.³⁵ These anion-derived inorganic SEI is corrosion resistant, thereby minimizing the continuous depletion of sodium and contributing to superior calendar aging performance.

Reduction tolerance of the electrolyte is also essential in determining interfacial stability, and therefore corrosion inhibition, at the hybrid anode. As depicted in Fig. 3k, the reduction potential of the NaFSI/DME-TTE electrolyte is approximately 0.05 V lower than that of NaPF₆/DME, which guarantees suppressed hybrid anode-electrolyte reactions.³⁶ Furthermore, the capacity loss was quantified in different electrolytes to evaluate the SEI solubility and stability (Fig. 3l).⁵ The SEI formed by the decomposition of the NaFSI/DME-TTE electrolyte leads to a smaller capacity loss (3.2 times lower than baseline electrolyte), indicating less SEI solubility and stronger passivation ability and effectively prevents continuous corrosion.

High voltage cathode and interphase

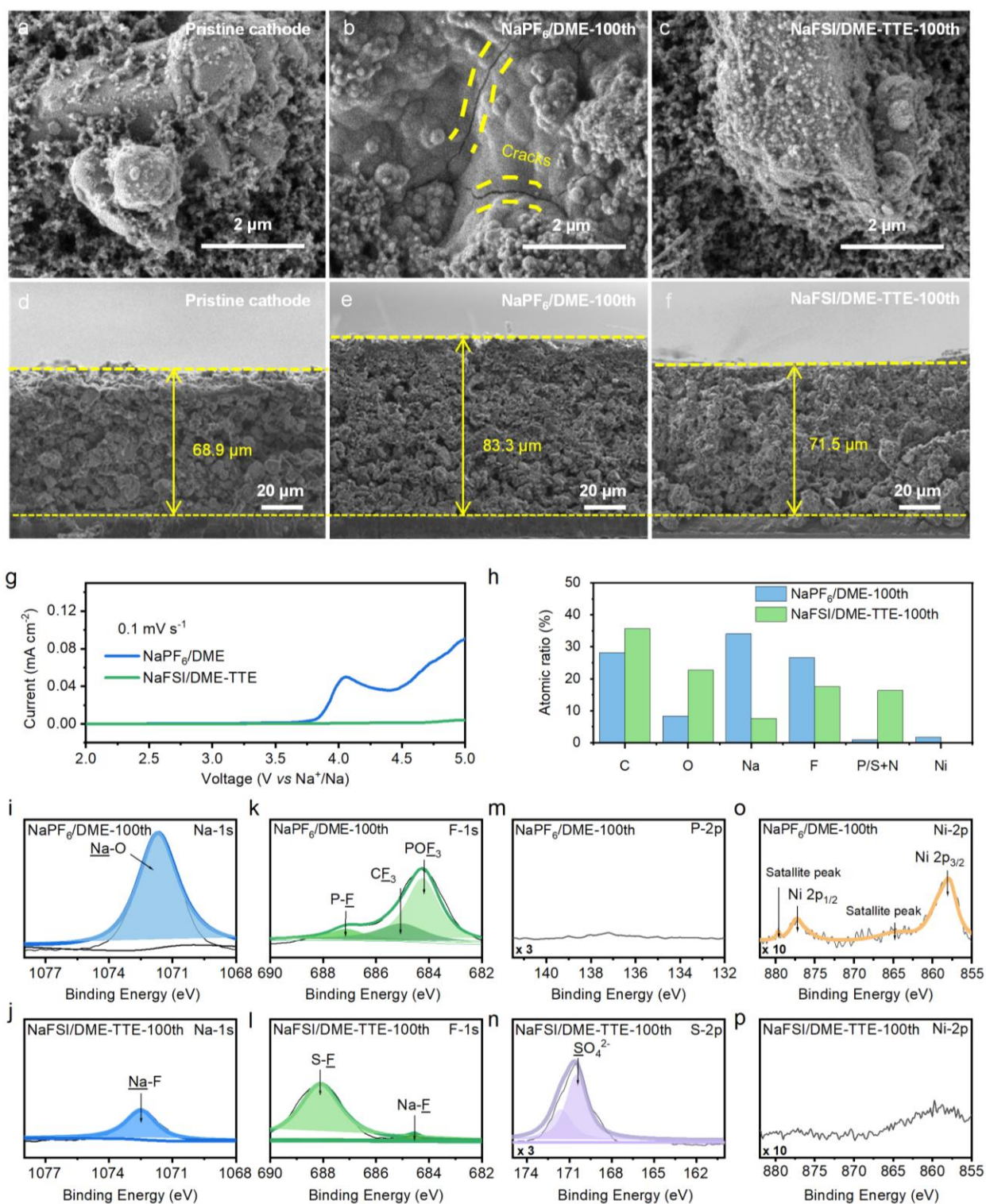


Figure 4. Characterizations of the NaMFN cathode with different electrolytes: (a-c) The morphology of pristine NaMFN cathode at initial state (a) and after 100 cycles (b: NaPF₆/DME

electrolyte; c: NaFSI/DME-TTE electrolyte); (d-f) The cross-sectional SEM images of the cathodes at initial state (d) and after 100 cycles (e: NaPF₆/DME electrolyte; f: NaFSI/DME-TTE electrolyte); (g) The oxidation stability of different electrolytes; (h) Atomic ratio of CEI generated in two electrolytes after 100 cycles; (i-p) The Na-1s, F-1s, P-2p, S-2p and Ni-2p XPS spectra with two electrolytes after 100 cycles.

Cathode interphase was further characterized to evaluate the high voltage stability of two electrolytes and compatibility with high voltage cathode. The morphology of the cathodes after 100 cycles exhibited substantial differences in two electrolytes. Compared to the pristine cathode (Fig. 4a), NaPF₆/DME electrolyte led to obvious cracks after 100 cycles (Fig. 4b, Fig. S5a), suggesting enlarged contact area between the electrode particles and the electrolyte, accelerating the dissolution of TMs. In contrast, the cathode retained a morphology similar to the pristine cathode in the NaFSI/DME-TTE electrolyte, with no obvious cracks observed (Fig. 4c, Fig. S5b). Furthermore, severe structural changes of cathode materials are often accompanied by substantial volume expansion.³⁶ Observed from the cross-section SEM images (Figs. 4d-f), the thickness of the cathode in the NaPF₆/DME electrolyte increased by 14.4 μm after cycling, leading to the separation and exfoliation of active materials, increased electron and Na⁺ diffusion resistance. In contrast, the cathode in the NaFSI/DME-TTE electrolyte showed a minimal increase in thickness (2.6 μm).

The high voltage stability of two electrolytes was verified by linear sweeping voltammetry (LSV). NaPF₆/DME electrolyte experiences significant oxidation before 4 V. In contrast, the

NaFSI/DME-TTE electrolyte remains stable up to 5 V, without notable oxidation or decomposition, demonstrating superior high voltage stability (Fig. 4g). This indicates that the NaFSI/DME-TTE electrolyte is compatible with high voltage cathode materials, leading to negligible change of crystal structure and electrode expansion.

The CEI composition after 100 cycles also showed significant variations (Figs. 4h-p, Figs. S6-S8). A higher proportion of inorganic CEI components was derived from anions decomposition in the NaFSI/DME-TTE electrolyte. Specifically, the content of the elements S and N is about 18 times that of P in the NaPF₆/DME. The CEI layer formed in the NaFSI/DME-TTE electrolyte is rich in NaF that can effectively impede electron tunneling and prevent CEI overgrowth, which is absent in the NaPF₆/DME electrolyte (Figs. 4i-4l).³⁷ The P-2p (Fig. 4m), S-2p (Fig. 4n), and N-1s (Fig. S8a) spectra in the two electrolytes confirmed that an inorganic CEI layer derived from anions was indeed formed on the cathode surface after cycling in NaFSI/DME-TTE. Moreover, no Ni-2p signal was detected in NaFSI/DME-TTE electrolyte, indicating the CEI formed in this anti-corrosion electrolyte can effectively suppress TM dissolution, while 1.72% Ni was detected in NaPF₆/DME electrolyte (Fig. 4h, Figs. 4o-p). In short, this stable, anion-derived inorganic CEI layer generated in the NaFSI/DME-TTE electrolyte preserves the overall cathode structure integrity, ensuring long-cycling stability of this high energy density hybrid Na battery. The scalability of the anti-corrosion interphase strategy was proved by a high concentration NaFSI/DME electrolyte (NaFSI:DME = 1:1.2, molar ratio) with anion-derived inorganic SEI for the uniform Na deposition, stable R_{ct} , and significantly improved cycling stability in the low N/P ratio Na@HC||NaMFN full cell.

In this study, we report an anti-corrosion ether-based electrolyte to address the parasitic corrosion of hybrid Na@HC anode towards Na batteries with exceptional stability even under stringent conditions (calendar aging and high voltage). By tuning the solvation structure of the electrolyte, we successfully build an anion-derived passivation interphase, effectively minimizing Na inventory loss by suppressed Na metal corrosion. Besides, this electrolyte also effectively mitigates cathode degradation, by alleviating cathode TM dissolution and structure cracks. As a result, hybrid Na batteries deploying the anti-corrosion electrolyte demonstrate excellent cycling stability, with 87.98% capacity retention and 99.82% average CE after 200 cycles at an N/P ratio of 1.91 and a practical cathode loading, compared to 3.59% capacity retention and 99.1% average CE in a conventional electrolyte. Furthermore, under the rigorous conditions of aging for 24 h every three cycles, the full cell using the anti-corrosion electrolyte still retained 81.19% capacity after 100 cycles, which is superior to the baseline electrolyte (eventually losing all reversible Na inventory after approximately 75 cycles). This work will not only aid further understanding of Na metal corrosion but also inspire future developments of high energy density Na batteries.

Experimental Methods

Electrolyte preparation

Battery grade sodium bis(fluorosulfonyl)imide (NaFSI) salt was purchased from Solvionic Co. (99.9%, France). Sodium hexafluorophosphate (NaPF₆) salt, 1,2-dimethoxyethane (DME) and 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE) were purchased from Duoduo Chem (99.9%, Suzhou, China) and dried with 4 Å molecular sieves (Sigma-Aldrich) for three days before use. The NaFSI/DME-TTE electrolyte was prepared with corresponding molar ratios [1:1.2:0.8].

The conventional ether-based electrolyte (1 M NaPF₆/DME) was prepared by dissolving 1 M NaPF₆ into DME. Electrolyte preparation was conducted inside an argon-filled glove box with H₂O, O₂ <0.01 ppm.

Electrode preparation

For hard carbon (HC) anode, HC (Kuraray Co.), conductive carbon, and polyvinylidene fluoride (PVDF) binder were mixed at a weight ratio of 85:8:7 and cast onto the Al current collector. Hybrid anodes were prepared using Na||HC half-cells. During the preparation process, the battery was first cycled at 0.1 C for three cycles, then cycled at 0.33 C for six cycles, and finally, the battery was terminated in a fully discharged state. For NaMn_{0.33}Fe_{0.33}Ni_{0.33}O₂ (NaMFN) cathode, it was prepared following our previous solid-state method.⁴ Then NaMFN, conductive carbon and PVDF were mixed at a weight ratio of 85:8:7 and coated onto the Al current collector. All electrodes were dried at 110 °C under vacuum for 12 h. For the hybrid anode, the areal loading of HC and sodium metal are around 1 mAh cm⁻² and 2 mAh cm⁻², respectively. The area loading for the NaMFN cathode is around 1.5 mAh cm⁻². The N/P ratio represents the total capacity of the hybrid anode (including Na metal and HC) divided by the cathode capacity.

Cell assembly

CR 2032-coin cells were assembled in an argon-filled glove box (O₂ <0.01 ppm and H₂O <0.01 ppm) to measure the electrochemical performance. For half-cells including Na||HC, Na@HC||Cu, Na||Al, Na||Cu and full-cells including Na@HC||NaMFN, 150 μL electrolyte was used per cell and the glass fiber (Whatman, D-type) was used as separator.

Electrochemical measurements

Linear sweeping voltammetry (LSV) and electrochemical impedance spectroscopy (EIS, frequency ranging from 0.01 Hz to 100 kHz with an alternating current voltage disturbance amplitude of 5 mV) were conducted with an electrochemical working station (Bio-logic SP-200). LSV was conducted to measure the electrochemical stability of different electrolytes using coin cells, with Al (for oxidation sweep) or Cu (for reduction sweep) as the working electrode and Na as the counter and reference electrodes. The scan rate is 0.1 mV s^{-1} . EIS was used to measure the impedance change of full-cells during cycling. A NEWARE battery testing system was used for evaluating GCD performance and long-term cyclability.

Characterization

Interfacial chemistries of SEI were analyzed by XPS (PHI 5000 VersaProbe III, Ulvac-Phi, Japan) with a monochromatic Al K α X-ray source (1486.6 eV). The binding energy values were all calibrated using the C-1s peak (284.8 eV). For the cycled electrodes, such as Na@HC after 100 cycles that require to conduct SEM and XPS, salt particles remaining on the surface of the electrodes need to be washed and removed with the corresponding solvent in the glove box. Then it is packaged in a container filled with argon and quickly transferred for testing.

ASSOCIATED CONTENT

Supporting Information

Supplementary data are available at ACS Energy Letters online.

Detailed information about CE and the XPS spectra of SEI and CEI, the SEM images of cycled cathodes.

AUTHOR INFORMATION

Yue Li: 602023770004@smail.nju.edu.cn

Minfei Fei: mf689@cam.ac.uk

Haiming Wang: realhaiming@163.com

Jianwei Hu: 502023340025@smail.nju.edu.cn

Huajie Zhang: 662023340005@smail.nju.edu.cn

Shujuan Han: hanshujuan2021@163.com

Jingyi Xiao: 652024770008@smail.nju.edu.cn

Xin Wang: 522024840008@smail.nju.edu.cn

Xujie Cheng: 652024770004@smail.nju.edu.cn

Manish Chhowalla: mc209@cam.ac.uk

Jia Zhu: jiazhu@nju.edu.cn

Yan Jin: yanjin@nju.edu.cn

NOTES

The authors declare no conflict of interest.

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