

Sodiophilic Fe/Na anodes enabling dendrite-free sodium metal batteries with ultralong cycle life

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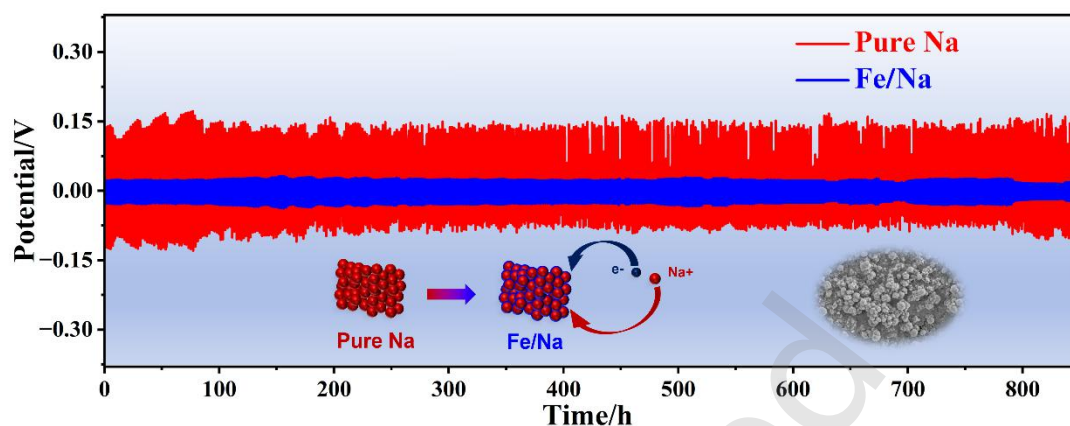
Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94908878>

<https://www.sciopen.com/journal/1998-0124> on May. 26, 2026

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A scalable one-step rolling strategy disperses sodiophilic Fe nanoparticles throughout a Na matrix, creating abundant uniform nucleation sites that reduce nucleation overpotential and accelerate charge transfer. The resulting Fe/Na alloy anode guides homogeneous, dendrite-free Na plating/stripping, delivering ultralong symmetric-cell stability (up to 850 h) and enabling high-rate, durable NVP||Fe-Na full cells.

Sodiophilic Fe/Na anodes enabling dendrite-free sodium metal batteries with ultralong cycle life

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Received: 9 March 2026; Revised: 30 April 2026; Accepted: 26 May 2026

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Cite this article: Nano Research, 2026, 19, 94908878 <https://doi.org/10.26599/NR.2026.94908878>

ABSTRACT: Sodium metal anodes hold great promise for next-generation high-energy batteries, yet practical deployment is hindered by severe dendrite growth and unstable electrode/electrolyte interfaces. Herein, we report a facile one-step rolling strategy to fabricate Fe/Na anodes, in which Fe nanoparticles are uniformly incorporated into the Na matrix to serve as sodiophilic nucleation sites. Structural analyses confirm the high purity, uniform dispersion, and improved surface integrity of the Fe/Na electrodes. Electrochemical measurements reveal a markedly reduced nucleation overpotential and enhanced charge-transfer kinetics, with a low activation energy of 26.87 kJ mol⁻¹ compared to pure Na (43.48 kJ mol⁻¹). As a result, Fe/Na||Fe/Na symmetric cells deliver exceptional cycling stability (850 h at 0.1 mA cm⁻² and 600 h at 0.5 mA cm⁻²), while full cells coupling Na₃V₂(PO₄)₃ cathodes exhibit excellent rate capability (73.7 mAh g⁻¹ at 10 C) and long-term retention (81% after 240 cycles at 5 C). Mechanistic investigations reveal that Fe incorporation effectively suppresses dendrite formation by promoting uniform Na deposition. This work provides both experimental and kinetic insights into alloy-based Na anodes, offering a scalable and cost-effective strategy for high-power, dendrite-free sodium metal batteries.

KEYWORDS: Fe/Na anode; sodium metal battery; dendrite suppression; nucleation overpotential; high-rate cycling; sodiophilic interface

1 Introduction

The rapid development of renewable energy technologies and the modernization of power transmission systems are fundamental to achieving high-efficiency energy utilization and enabling the transition towards a sustainable energy future [1-3]. Energy storage devices, in particular, play a pivotal role in mitigating the intermittency of renewable energy sources while satisfying the continuously increasing global energy demand and alleviating environmental concerns. However, insufficiently mature energy storage and transmission technologies may lead to further energy loss and inefficiency, underscoring the urgent need for reliable devices capable of storing and delivering energy in a controllable and efficient manner. Among emerging energy storage devices, lithium-ion batteries (LIBs) have dominated various applications, such as pure electric vehicles and hybrid electric vehicles, due to their high energy density, extended cycle life, and environmental friendliness [4-8]. Nevertheless, the uneven distribution of lithium resources, poor low-temperature performance, and potential safety hazards remain formidable challenges, especially for large-scale applications [9-12]. Consequently, the development of alternative energy storage systems that circumvent the

limitations of LIBs has become a pressing scientific priority [13]. Sodium-ion batteries (SIBs) have attracted considerable attention because of several intrinsic advantages that address the shortcomings of LIBs: (i) abundant resources and low cost, as sodium is widely distributed in the Earth's crust; (ii) superior low-temperature performance, enabling stable operation over a wide temperature range (-40 °C to 80 °C); and (iii) enhanced safety due to lower sensitivity of electrolytes and separators to high temperatures, significantly reducing the risk of thermal runaway [14]. These attributes indicate that SIBs could serve as a highly promising alternative to LIBs for large-scale energy storage and high-power applications. The electrochemical performance of SIBs is strongly dependent on the properties of the anode. Conventional SIBs anode materials can be broadly classified into insertion-type (carbonaceous materials [15-18]), conversion-type (metal sulfides and oxides [19-21]), and alloy-type materials [22], depending on their sodium storage mechanisms. Insertion-type anodes usually display high structural stability, satisfactory cycling performance, and cost-effective scalability, but suffer from low theoretical capacities and sluggish ion diffusion kinetics. Conversion-type anodes offer higher capacities yet experience substantial volume changes, unstable cycling, and poor electronic conductivity. Alloy-type anodes combine high capacity with decent rate

capability but undergo severe volume expansion during alloying/dealloying, causing electrode pulverization and unstable solid electrolyte interphase (SEI) formation [23, 24]. These inherent limitations call for the exploration of new anode materials with improved sodium storage capability, cycling stability, and safety characteristics.

Metallic sodium, by virtue of its extremely high theoretical capacity (1165 mAh g^{-1} , nearly three times that of metallic lithium) and low electrochemical potential, has emerged as an ideal anode candidate for rechargeable sodium batteries [25]. Compared to conventional hard-carbon anodes ($\sim 372 \text{ mAh g}^{-1}$), sodium metal enables much higher energy densities [26–28]. Moreover, the cooperative reaction between metallic sodium and liquid electrolytes can generate an SEI layer containing inorganic components with enhanced flexibility and conductivity. Additionally, sodium metal electrodes are environmentally benign and free of toxic heavy metals. Despite these advantages, sodium metal is plagued by severe dendrite growth and instability of the solid electrolyte interphase (SEI) film [29]. The SEI typically contains abundant organic components with insufficient mechanical strength and poor ionic conductivity, leading to repeated fracture under deposition-induced stress. This fracture exposes fresh sodium surfaces and triggers continuous side reactions, resulting in a detrimental “fracture-regeneration” cycle that compromises cycling stability. To address these issues, several strategies have been investigated, including alloying, electrolyte optimization, and the use of porous carbon scaffolds. Alloying is particularly attractive as it can stabilize the electrode structure, suppress dendrite formation, mitigate volume expansion, and produce a denser and more flexible SEI, thereby enhancing Coulombic efficiency and rate capability [30–33]. For instance, a multiphase artificial interphase layer composed of NaBi_3 alloy and NaCl has been shown to lower the Na^+ diffusion barrier, induce uniform Na deposition and enable symmetric cells to achieve stable cycle performance [34]. However, the mechanical degradation of sodiophilic coatings under repeated volume changes remains a concern [35, 36]. Unlike conventional alloy-based or single-component sodiophilic coatings, the iron-based system offers chemical passivation to prevent further Na reduction, accommodates Na^+ within the interphase itself, and reduces the local current density at the electrode interface [37]. Moreover, the incorporation of iron components further homogenizes the electric field distribution and suppresses dendrite initiation [38].

Based on these considerations, the present work proposes a facile one-step rolling approach to fabricate a Fe/Na anode, aiming to achieve uniform sodium nucleation and deposition. The Fe/Na electrode exhibits a reduced nucleation overpotential, indicating high sodium affinity, thereby promoting uniform Na^+ nucleation and deposition and effectively suppressing dendrite formation. Electrochemical evaluations reveal that Fe/Na||Fe/Na symmetric cells deliver a remarkably long cycling lifetime of $\sim 600 \text{ h}$ under 0.5 mA cm^{-2} plating/stripping conditions. Furthermore, when assembled with a $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) cathode, the NVP||Fe/Na full cell demonstrates outstanding rate capability and cycling stability, sustaining over 240 cycles at 5 C with high-capacity retention of 81%. This study provides valuable experimental evidence and theoretical insights into designing low-cost, high-performance sodium metal battery

anodes.

2 Experimental

2.1. Preparation of Fe/Na anodes

Metallic sodium (purity $\geq 99.9\%$) and iron powder (purity $\geq 99.5\%$, particle size $\sim 10 \mu\text{m}$) were purchased from commercial suppliers and used without further purification. A small block of metallic sodium was first mechanically cleaned to remove the surface oxide layer. The sodium was then sealed in a plastic bag and rolled into thin sheets using a rolling press inside the glovebox. Circular sodium discs with a diameter of 10 mm were obtained using a disc cutter. For preparing Fe/Na anodes, sodium sheets were mixed with iron powder in a mass ratio of 1:0.25, followed by repeated rolling to ensure uniform dispersion of Fe particles within the sodium matrix. The composite sheets were subsequently punched into 10 mm diameter electrodes using the same disc cutter. All operations involving metallic sodium were conducted in an Argon-filled glovebox ($\text{O}_2 < 0.1 \text{ ppm}$, $\text{H}_2\text{O} < 0.1 \text{ ppm}$) to prevent oxidation and moisture contamination.

2.2 Structural characterization

The crystalline structures of the prepared electrodes were analyzed by X-ray diffraction (XRD, $\text{Cu K}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$). The composition and chemical states were examined via X-ray photoelectron spectroscopy (XPS) with $\text{Al K}\alpha$ excitation. Surface morphologies were observed using scanning electron microscopy (SEM) operated at 5 kV acceleration voltage.

2.3 Electrochemical measurements

Symmetric cells were assembled in the sequence: stainless steel case - sodium (or Fe/Na) disc - glass fiber separator - sodium (or Fe/Na) disc - spacer - spring - stainless steel case. Two drops of electrolyte (1 M NaPF_6 in Dimethoxyethane (DME)) were added directly onto the separator to ensure full wetting. The cells were hermetically sealed using a CR2032 coin-cell crimping machine inside the glovebox. Sodium vanadium phosphate ($\text{Na}_3\text{V}_2(\text{PO}_4)_3$, abbreviated as NVP) cathode material was synthesized via a conventional solid-state method as described in our previous study. Polyvinylidene fluoride (PVDF), acetylene black (AB), and N-methyl-2-pyrrolidone (NMP) were obtained from Aladdin Reagent Co., Ltd. The NVP cathode slurry was prepared by mixing 70 wt% NVP powder, 20 wt% acetylene black, and 10 wt% PVDF binder in NMP solvent, followed by continuous stirring for 24 h to obtain a homogeneous suspension. The slurry was uniformly coated on aluminum foil (10 mm diameter) using a doctor blade and dried in a vacuum-drying oven at $60 \text{ }^\circ\text{C}$ for 10 h. The mass of active material was determined by subtracting the mass of bare Al foil from the coated electrode mass. The full cells were assembled with NVP as the cathode and Fe/Na electrode as the anode. The same electrolyte and coin-cell configuration were used. Galvanostatic plating/stripping cycles for symmetric cells were performed using a battery testing system (Neware, Shenzhen, China) at various current densities ($0.1\text{--}3 \text{ mA cm}^{-2}$). The overpotential for sodium nucleation was determined from the initial stage of plating/stripping voltage profiles. Electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements were conducted on an electrochemical workstation (Gamry Instruments) in the frequency range of 100 kHz to 0.01 Hz with an amplitude of 5

mV. Full-cell tests (NVP||Fe/Na) were carried out at 0.1-10 C rates to evaluate cycling performances.

3 Results and discussion

The crystalline structure of the as-prepared Fe/Na electrodes was first examined by X-ray diffraction (XRD) (**Fig. 1a**). The diffraction peaks located at $2\theta = 29.477^\circ$, 42.174° , 44.474° , 52.29° , 61.196° , 65.022° , and 69.342° correspond well to the standard reflections of metallic Na and Fe, with no detectable impurity phases. This confirms the high purity of the Fe/Na

electrode and suggests a well-developed crystallinity. In addition to XRD, X-ray photoelectron spectroscopy (XPS) was employed to determine the chemical states (**Fig. 1b** and **Fig. S1**). The high-resolution Na 1s spectrum shows a characteristic peak at 1071.5 eV, indicating the presence of metallic sodium, while the Fe 2p spectrum displays a prominent peak at 706.8 eV, attributable to metallic Fe. These results collectively confirm the successful incorporation of Fe into the Na matrix without the formation of undesirable compounds.

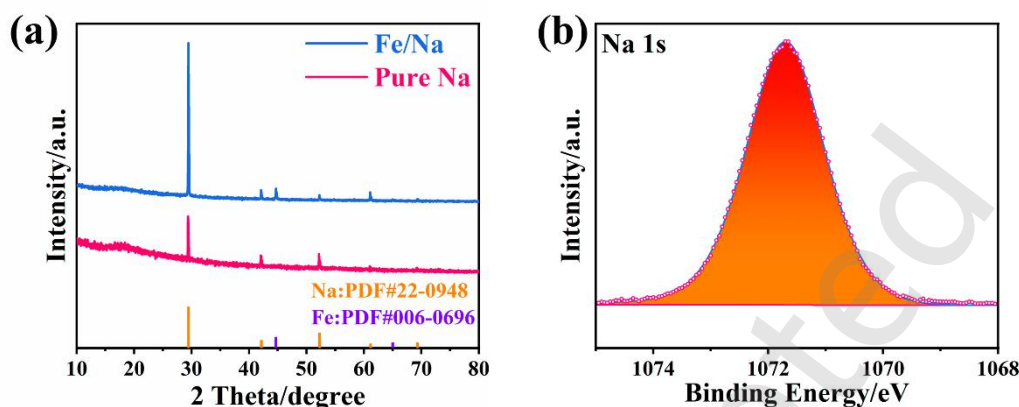


Fig. 1. (a) XRD patterns of pure Na and Fe/Na anodes; (b) High - resolution XPS spectrum of Na 1s.

The surface morphology of pure Na and Fe/Na electrodes was investigated via SEM (**Fig. 2**). Pure Na exhibits irregular particles with noticeable cracks, which can act as preferential sites for dendrite initiation. In contrast, Fe/Na electrodes present a densely packed granular structure with a relatively smooth surface, indicative of enhanced mechanical integrity. The uniform dispersion of Fe throughout the Na matrix is expected to optimize nucleation sites and mitigate localized current densities during plating.

The sodium plating/stripping behavior using Na||Na and Fe/Na||Fe/Na symmetric cells. The nucleation overpotential profiles (**Fig. 3a**) reveal that Fe/Na electrodes exhibit a significantly lower initial overpotential than pure Na, suggesting an intrinsically higher Na affinity. During prolonged cycling, the polarization overpotential of Fe/Na electrode remains consistently lower than that of pure Na, demonstrating improved charge-transfer kinetics and reduced interfacial resistance due to the presence of Fe. The galvanostatic cycling stability is shown in **Fig. 3b**. At 0.1 mA cm^{-2} , Fe/Na||Fe/Na cells sustain stable operation for $\sim 850 \text{ h}$, far exceeding the lifetime of Na||Na cells and symmetric cells reported in recent literatures (e.g., 167 h for the Na-Ni foam||Na-Ni foam [39]; $\sim 300 \text{ h}$ for the $\text{Na}_3\text{Bi}@Na||\text{Na}_3\text{Bi}@Na$ [40]; 446 h for the $\text{Na}_7\text{Zn}_{13}@Na||\text{Na}_7\text{Zn}_{13}@Na$ [41]; $\sim 600 \text{ h}$ for $\text{Na}@Na^+\text{-intercalated montmorillonite (Na-MMT)}||\text{Na}@Na\text{-MMT}$ [42]). Furthermore, rate capability tests (**Fig. 3c**) indicate that Fe/Na electrodes maintain low voltage hysteresis across a wide current density range ($0.1\text{-}0.5 \text{ mA cm}^{-2}$). Remarkably, when the current

density is reverted from 0.5 mA cm^{-2} to 0.1 mA cm^{-2} , the voltage profile of the Fe/Na||Fe/Na cell quickly recovers to its initial plateau, signifying excellent reversibility. Even under high current density (0.5 mA cm^{-2}), Fe/Na||Fe/Na cells exhibit robust cycling over 600 h with minimal voltage drift (**Fig. 3d**), whereas Na||Na cells suffer from severe polarization and rapid degradation. Here, the first five cycles were conducted at low current densities of 0.1 mA cm^{-2} to activate the Fe/Na electrode material. These symmetric - cell results provide compelling evidence that Fe incorporation fundamentally enhances the sodium plating/stripping behavior by simultaneously lowering the nucleation overpotential, reducing interfacial polarization, and sustaining stable voltage profiles over extended cycling. The ultralong lifespan of the Fe/Na||Fe/Na cells, their minimal hysteresis across a broad current range, and the rapid recovery to the original voltage plateau upon current reversal collectively indicate highly reversible Na deposition and stripping processes. Even under aggressive operating conditions of high current density, the Fe/Na electrodes maintain structural and electrochemical integrity, in stark contrast to the rapid performance decay observed in pure Na electrodes. Taken together with the morphological observations and kinetic analyses presented earlier, these results confirm that sodiophilic Fe sites and the dense microstructure work synergistically to promote uniform Na nucleation, facilitate rapid charge transfer, and suppress dendrite formation, thereby delivering both exceptional rate capability and unprecedented cycling stability in sodium - metal anodes.

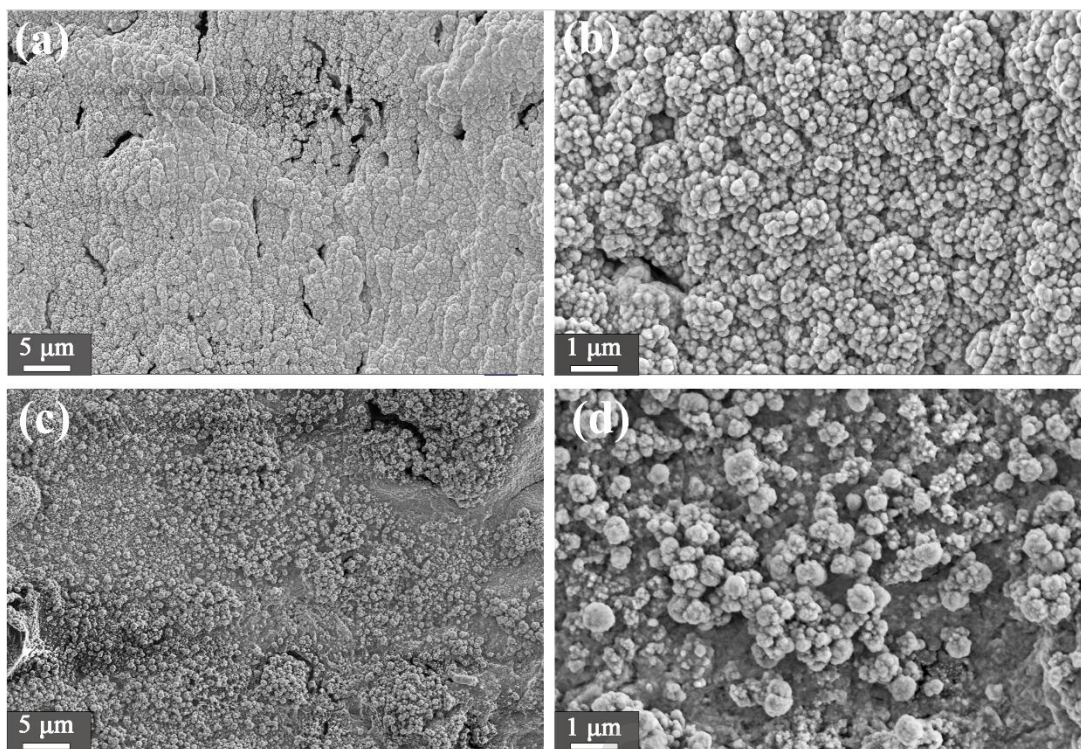


Fig. 2. SEM images of pure Na metal anode (a, b) and Fe/Na anode (c, d).

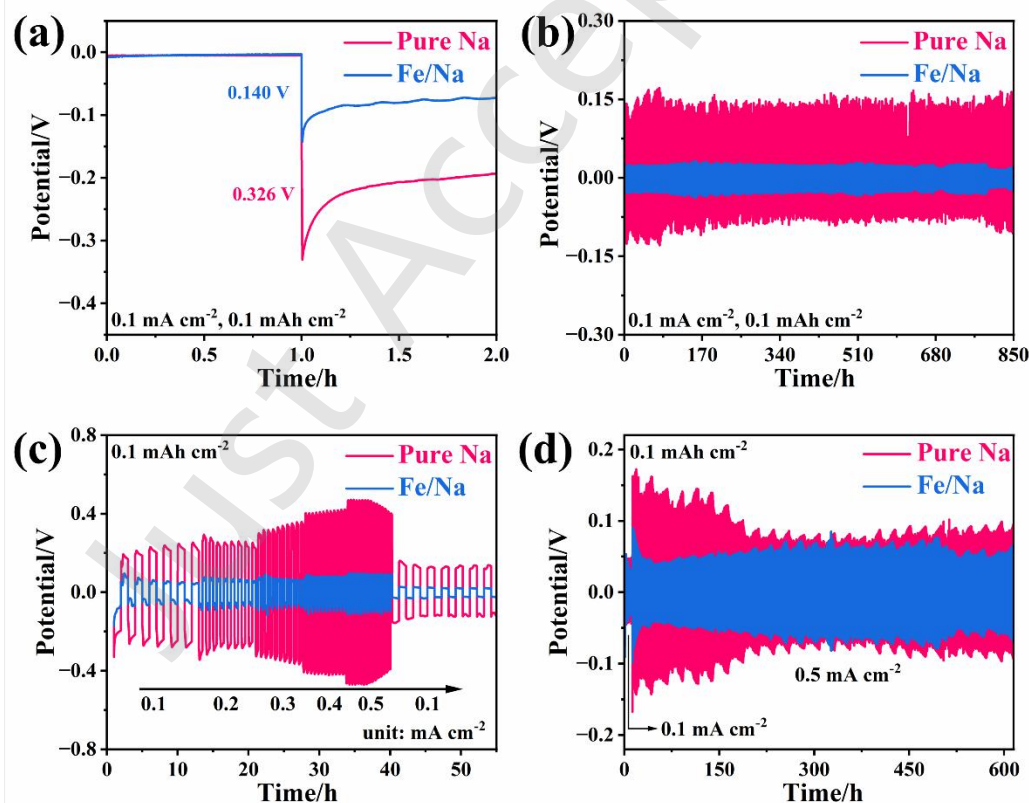


Fig. 3. The electrochemical performance of Fe/Na||Fe/Na and Na||Na symmetric cells. (a) Nucleation overpotential; (b) Cycling performance at 0.1 mA cm^{-2} ; (c) Rate capability; (d) Cycling performance at 0.5 mA cm^{-2} .

To further demonstrate the effectiveness of iron incorporation in stabilizing the plating/stripping cycles, the cycling performance of pure Na and Fe/Na symmetrical cells were compared under higher current densities (Fig. S2). When the current density was increased to 1 mA cm^{-2} with an areal capacity of 1 mAh cm^{-2} , the pure Na electrode exhibited a large polarization voltage

($\sim 0.407 \text{ V}$) and pronounced voltage fluctuations. This phenomenon was likely attributable to the formation of dendrites caused by uneven Na deposition, ultimately leading to degradation of the sodium storage performance. In stark contrast, the Fe/Na symmetrical cells achieved stable plating/stripping cycles with a low nucleation overpotential (~ 0.244) and no

significant change in polarization voltage (Fig. S2a, b). Even at a current density of 3 mA cm^{-2} , the Fe/Na electrode showed only a negligible increase in nucleation overpotential (Fig. S2c), and the polarization voltage remained below 200 mV (Fig. S2d). These results indicate that, even under high current densities, metallic iron can promote uniform Na deposition and suppress Na dendrite formation during the Na plating process, thereby effectively enhancing the cycling stability of Na plating/stripping and endowing the Fe/Na electrode with outstanding electrochemical performance.

The sodium deposition kinetics of Fe/Na and pure Na electrodes were systematically investigated using Tafel analysis and electrochemical impedance spectroscopy (EIS), as shown in Fig. 4 and Tab. S1. In the Tafel plots (Fig. 4a), the Fe/Na electrode exhibits a much higher exchange current density ($\sim 0.081 \text{ mA cm}^{-2}$) compared to pure Na ($\sim 0.015 \text{ mA cm}^{-2}$), reflecting significantly accelerated interfacial charge-transfer kinetics [43]. This enhancement is attributed to the presence of sodiophilic Fe sites, which lower the nucleation overpotential, stabilize the initial Na adatoms, and promote rapid and uniform deposition. Consistently, EIS measurements (Fig. 4b) across a

temperature range of 25°C to 40°C reveal that Fe/Na electrodes possess substantially smaller charge-transfer resistance (R_{ct}) values, decreasing from 106Ω at 25°C to 28Ω at 40°C , whereas pure Na electrodes (Fig. 4c), in contrast, show much larger resistances from 745Ω to 298Ω . The lower R_{ct} values indicate a more conductive and chemically stable electrode/electrolyte interface in the Fe/Na electrodes, ensuring efficient electron and ion transport even under elevated temperatures that typically aggravate non-uniform growth [44]. By fitting the temperature-dependent R_{ct} to the Arrhenius equation, the apparent activation energy (E_a) (Fig. 4d) for Na deposition on Fe/Na electrodes was determined to be $26.87 \text{ kJ mol}^{-1}$, which is markedly lower than that on pure Na ($43.48 \text{ kJ mol}^{-1}$). The reduced activation barrier allows Na^+ to deposit with minimal energetic cost, resulting in dense and uniform layers instead of localized, high-field protrusions. Mechanistically, this is associated with the facilitation of homogeneous nucleation by Fe atom sites and the improvement in electron conductivity and Na^+ diffusion afforded by the dense microstructure, which together suppress dendrite formation and maintain low polarization throughout cycling.

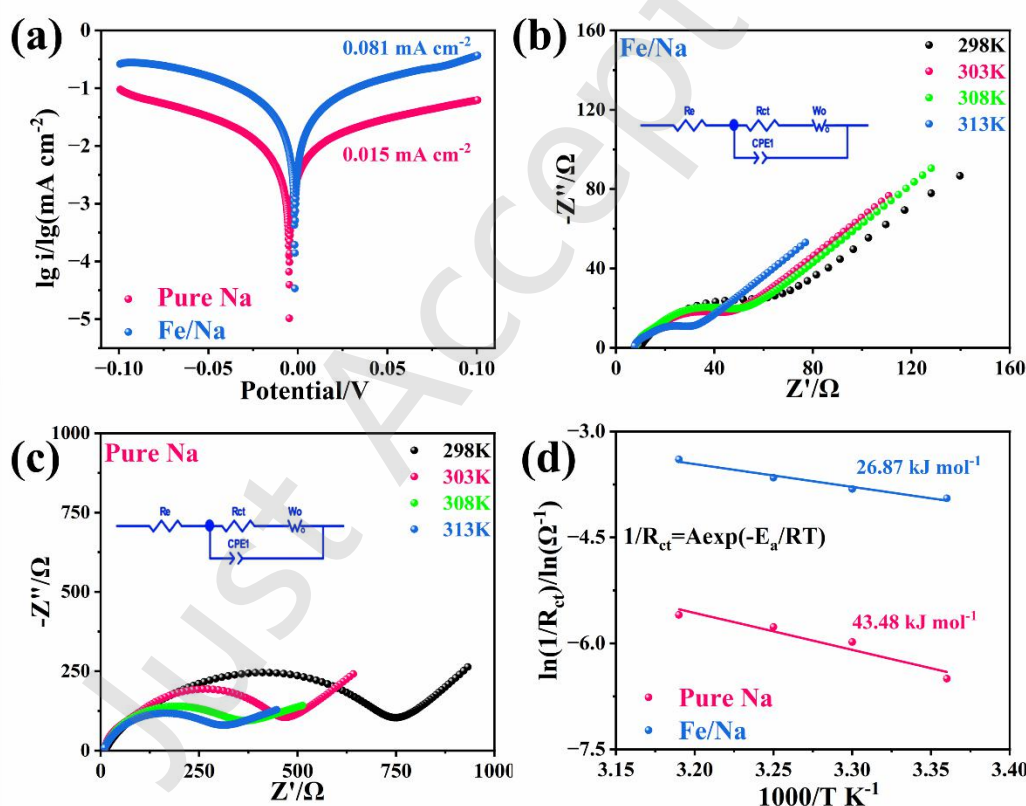


Fig. 4. (a) Tafel plots of Fe/Na||Fe/Na and Na||Na symmetric cells; (b, c) EIS curves and corresponding equivalent circuit models at different temperatures; (d) Activation energy plots.

In order to further demonstrate the effectiveness of the Fe/Na anode in regulating sodium deposition behavior, quartz symmetric cells with transparent windows were employed for in-situ optical observation of the sodium plating process on Fe/Na and pure Na electrodes, as shown in Fig. 5. At the initial stage, both electrodes exhibited a relatively flat surface without obvious sodium dendrites. After 15 minutes of plating, small protrusions began to appear on the pure Na surface, which gradually evolved into needle-like dendrites over time.

Following 30 minutes, the pure Na electrode was largely covered by irregular sodium deposits. After 60 minutes, severe and localized dendritic growth dominated the entire surface. In sharp contrast, the Fe/Na composite electrode maintained a uniform and flat deposition morphology throughout the entire plating process. This clearly indicates that the introduction of Fe into the Na anode effectively suppresses the formation of localized massive sodium dendrites, promoting a more homogeneous sodium flux and stable interfacial evolution.

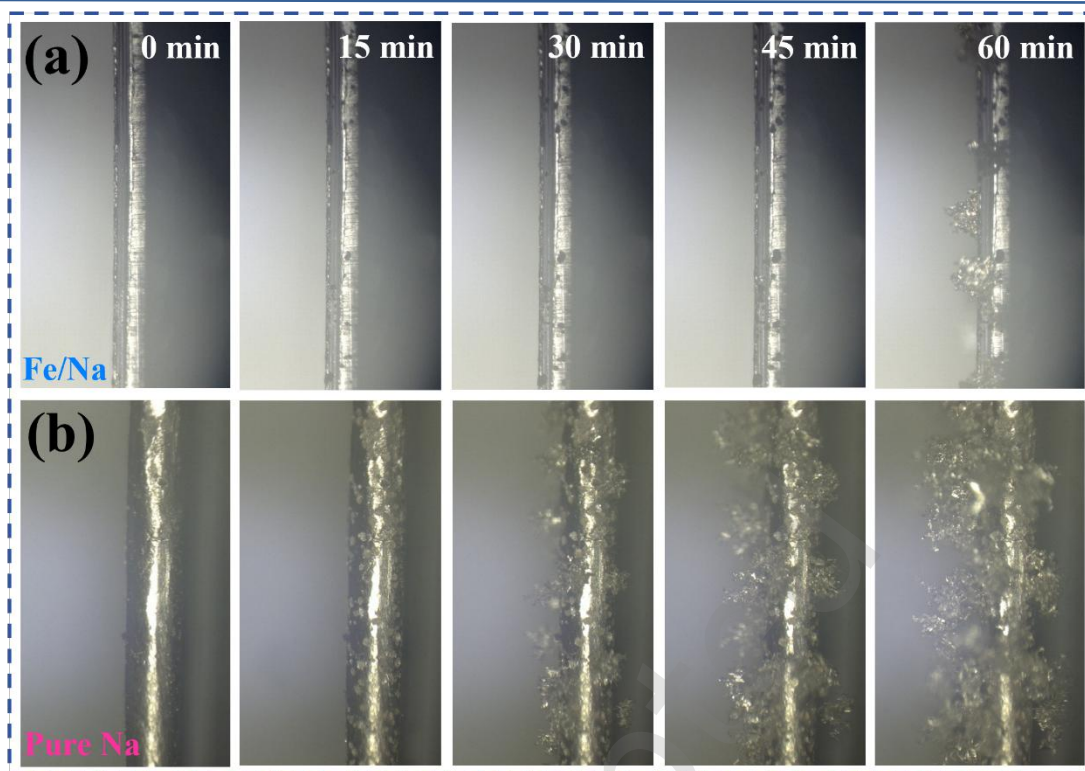


Fig. 5. In-situ optical images of Na deposition process for pure Na (a) and Fe/Na anode (b) at 0.5 mA cm^{-2} with a fixed capacity of 0.5 mAh cm^{-2} .

To evaluate the practical feasibility of the Fe/Na anode in realistic battery configurations, the NVP cathode was paired with the Fe/Na anode to assemble full cells. As shown in **Fig. 6a**, the NVP||Fe/Na full cell delivers an initial discharge capacity of 118.8 mAh g^{-1} (calculated based on the active mass of the NVP cathode) at a low rate of 0.1 C . The cyclic voltammetry (CV) measurements were tested to demonstrate the electrochemical reaction kinetics of the NVP||Fe/Na full cell. The CV profiles shown in **Fig. S3** holds the exhibited two redox peaks at 3.3 V and 3.5 V , corresponding to the sodium-ion insertion/extraction process in NVP, which is in excellent agreement with the results obtained from the galvanostatic charge–discharge profiles. And the approximately coincident CV curves also proves the high reversibility of the devices. Remarkably, the capacity retention of the full cell remains $\sim 91.3\%$ after 100 continuous cycles at 0.1 C (**Fig. 6b**), indicating exceptionally stable electrochemical behavior under prolonged operation. Compared with cells using pristine Na metal anodes, the Fe/Na electrode configuration suppresses interfacial degradation and parasitic side reactions, which are often responsible for capacity fading in conventional systems. The rate performance shown in **Fig. 6c-d** further confirms the superior kinetics enabled by the Fe/Na electrodes. Even when the current rate is increased to 8 C and 10 C , the full cell still maintains discharge capacities of 81.9 and 73.7 mAh g^{-1} , respectively. This outstanding rate capability originates from the sodiophilic Fe/Na interface that facilitates rapid Na^+ transport and uniform plating/stripping, effectively minimizing polarization during high - rate operation. Moreover, the

mechanical robustness of the rolled microstructure accommodates repeated Na deposition and removal without triggering dendrite formation, thereby preserving electrode integrity.

Long - term cycling at 5 C (**Fig. 6e**) demonstrates the durability of the system with a capacity retention of 81% after 240 cycles, which is also surpasses that of many full cells, e.g., NVP||Na@Ca²⁺-intercalated montmorillonite device ($\sim 43\%$ at 2 C after 200 cycles) [42], NVP||polytetrafluoroethylene-Na ($\sim 80\%$ at 2 C after 200 cycles) [45], etc.. The galvanostatic charge-discharge curves also shows the general shape with a stable platform under different cycle times in **Fig. S4**. Such stability under large current densities is rarely achieved in Na - metal systems, especially when considering the high cathode utilization and low interfacial resistance observed here. This performance suggests that the Fe/Na anode not only extends cycle life but also enables high - power sodium - metal batteries, making it a strong candidate for large - scale stationary energy - storage applications where fast charge/discharge capability and safety are critical. Overall, the full - cell results validate that the combination of scalable rolling fabrication, improved nucleation behavior, and dendrite suppression in the Fe/Na electrode directly translates into high - rate and long - lifespan operation in practical device architectures. This provides a clear pathway for transitioning sodium - metal technology from laboratory demonstrations to industrial - scale deployment in renewable - energy storage systems.

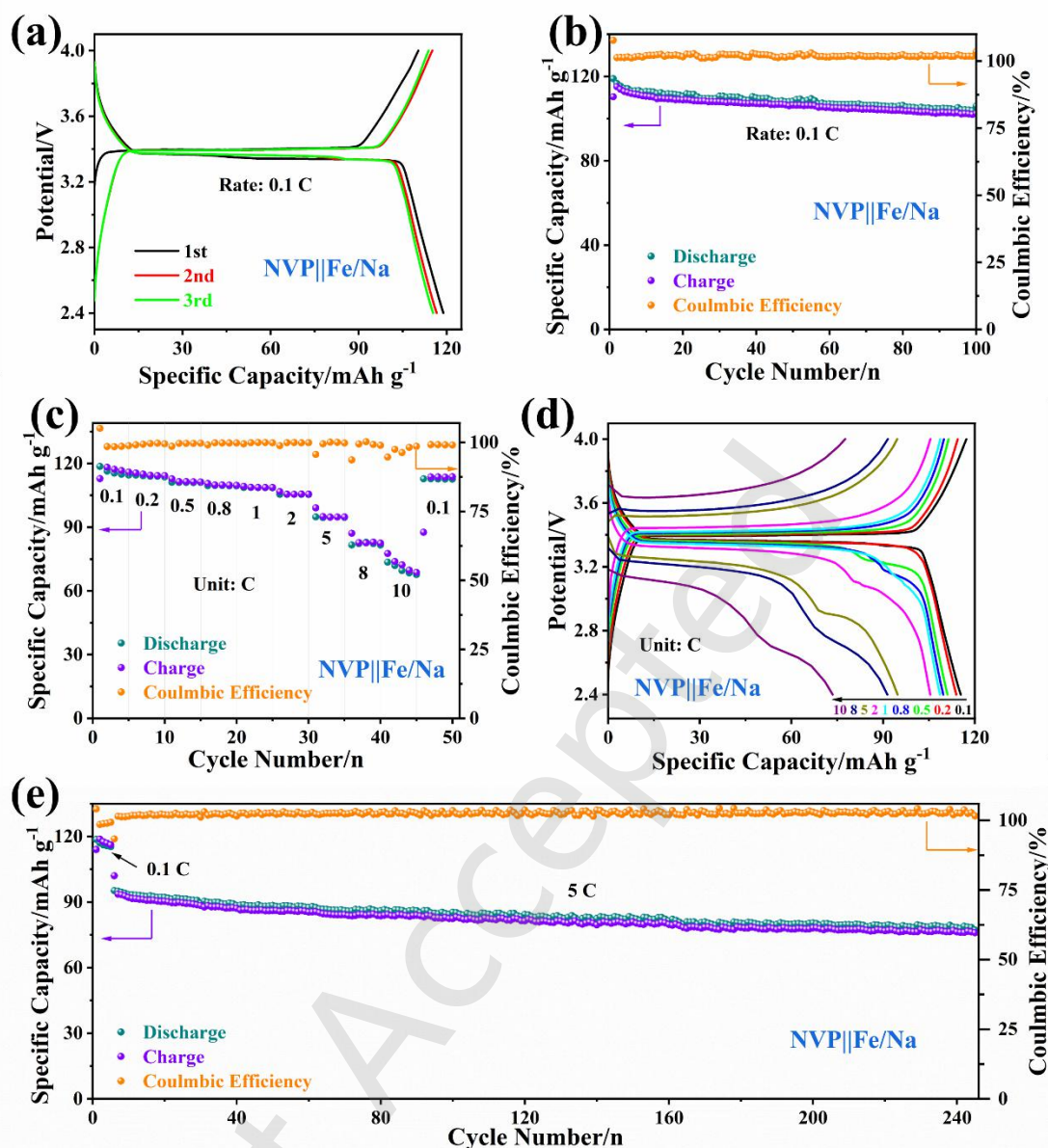


Fig. 6. The electrochemical performance of NVP||Fe/Na full cells. (a) Charge/discharge voltage-specific capacity profiles at 0.1 C; (b) Cycling performance at 0.1 C; (c) Rate capability; (d) Charge/discharge profiles at various C - rates; (e) Cycling performance at 5 C.

The markedly enhanced cycling stability observed for Fe/Na electrodes can be ascribed to the synergistic effects of their unique metallic microstructure and optimized electrode/electrolyte interfacial chemistry. Post - cycling XRD characterization (**Fig. S5**) shows that the Fe/Na electrode retains its original phase composition even after 100 repeated plating/stripping cycles, with no detectable formation of secondary phases or significant peak broadening. This preservation of crystallographic integrity strongly suggests that the framework efficiently accommodates the volumetric changes associated with Na insertion/extraction, thereby mitigating mechanical stress and preventing pulverization [33]. Detailed SEM observations (**Fig. S6**) provide direct morphological evidence of this stability. The Fe/Na surface remains dense and smooth after cycling, lacking the protrusions, whisker - like dendrites, or “dead” Na deposits commonly observed on pristine Na electrodes. Energy-dispersive X-ray spectroscopy elemental mappings further confirm that Na and Fe are uniformly

distributed across both the electrode surface and cross-section (**Fig. S7**). This smooth and compact surface configuration optimizes the electric field distribution and ion flux pathways, promoting the formation of a uniform and dense Na deposition layer while mitigating mechanical stress and volume variations during charge/discharge processes. These results clearly validate the superior performance of the as-constructed SEI interlayer in enhancing the cycle life and operational stability of the Na metal anode. In stark contrast, pure Na electrodes display pronounced surface cracking, irregular and porous deposits, and extensive morphological degradation, all of which are indicative of uncontrolled Na nucleation and growth during cycling. Such degradation in pure Na electrodes is known to increase local current density, disrupt SEI uniformity, and foster the formation of electrically isolated Na, thereby accelerating capacity decay and safety risks.

In addition, EIS was also employed to evaluate the interfacial stabilization of the Fe/Na electrode. As illustrated in **Fig. S8a**, the diameter of the semicircle observed for the Fe/Na anode is

distinctly smaller than that of the pure Na anode, indicating a lower R_{ct} for the Fe/Na electrode. This result demonstrates that the incorporation of Fe leads to a notable reduction in the R_{ct} of the Na anode. With increasing cycle number, the R_{ct} values of both anodes rise, however, the Fe/Na electrode exhibited a comparatively minor variation in R_{ct} (Fig. S8b). This indicates that, whilst stabilizing the interface, the addition of Fe not only enhances the electrical conductivity of the Na anode but also accelerates the charge-transfer process.

The incorporation of Fe into the sodium metal plays a pivotal role in these improvements. As a sodiophilic transition metal, Fe exhibits a strong binding affinity for Na atoms, acting as preferential nucleation sites that lower the energy barrier for initial Na deposition. Specifically, the metallic Fe sites promote homogeneous sodium nucleation and growth by effectively redistributing the local current density across the electrode surface. The Fe component also enhances electronic conductivity in the near-surface region, while the resulting Fe/Na interfaces provide fast pathways for Na^+ diffusion [46]. Moreover, iron demonstrates a higher exchange current density, indicating accelerated charge-transfer kinetics that further facilitate efficient Na^+ migration, thereby boosting the sodium storage performance [47]. Beyond kinetic benefits, metallic iron stabilizes the electrode interface, suppresses parasitic reactions between the electrolyte and the electrode, and effectively inhibits sodium dendrite growth [48]. Unlike conventional alloy-based or single-component sodiophilic coatings, this iron-based system offers chemical passivation to prevent further Na reduction, accommodates Na^+ within the interphase, and reduces the local current density at the electrode interface [38]. Such combined effects suppress tip-enhanced electric fields, a key origin of dendrite formation, resulting in a self-regulated deposition process that evolves into a compact and uniform Na layer during cycling [49]. Together, the structural stability confirmed by XRD and the dendrite-free morphology observed in SEM underscore the robustness of the Fe/Na interface in repeated plating/stripping operations. These findings not only explain the superior cycling performance of Fe/Na electrodes reported in symmetric cell and full-cell tests, but also validate the alloy-engineering strategy as an effective means to simultaneously address the mechanical, electrochemical, and safety challenges of sodium-metal anodes [30, 31].

4 Conclusions

In summary, a facile one-step rolling strategy was developed to fabricate Fe/Na anodes for high-performance sodium metal batteries. The introduction of Fe into metallic Na significantly reduces the nucleation overpotential, enhances Na affinity, and facilitates uniform Na^+ deposition, thereby effectively suppressing dendrite formation. The Fe/Na exhibits superior structural stability and fast charge-transfer kinetics, as evidenced by a low activation energy ($26.87 \text{ kJ mol}^{-1}$) compared to pure Na ($43.48 \text{ kJ mol}^{-1}$). Consequently, Fe/Na||Fe/Na symmetric cells achieve outstanding cycling stability, maintaining operation for over 850 h at 0.1 mA cm^{-2} and 600 h at 0.5 mA cm^{-2} . In full-cell configuration with a $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathode, the NVP||Fe/Na battery delivers excellent rate capability (73.7 mAh g^{-1} at 10 C) and long-term stability, with 81% capacity retention after 240 cycles at 5 C . This work not only provides experimental

evidence and a mechanistic understanding of sodiophilic interfaces but also offers a low-cost and scalable approach for designing dendrite-free, long-lifespan, and high-power sodium metal batteries. Future studies may further optimize sodiophilicity and microstructure to enable large-scale applications in grid-level energy storage and high-rate power systems.

Electronic Supplementary Material: Supplementary material (please provide the brief detail of the ESM) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908878>.

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by the Natural Science Foundation of Shandong Province (No. ZR2023QB011, ZR2025MS901 and ZR2025QC603), the National Natural Science Foundation of China (No. 52302260, 52504056, and 52404321), the PhD early development program of Liaocheng University (No. 318052134), China Postdoctoral Science Foundation (No. 2025M782974), and Postdoctoral Fellowship Program of CPSF (No. GZC20251943).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Just Accepted

Electronic Supplementary Material

Sodiophilic Fe/Na anodes enabling dendrite-free sodium metal batteries with ultralong cycle life

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Supporting information to <https://doi.org/10.26599/NR.2026.94908878>

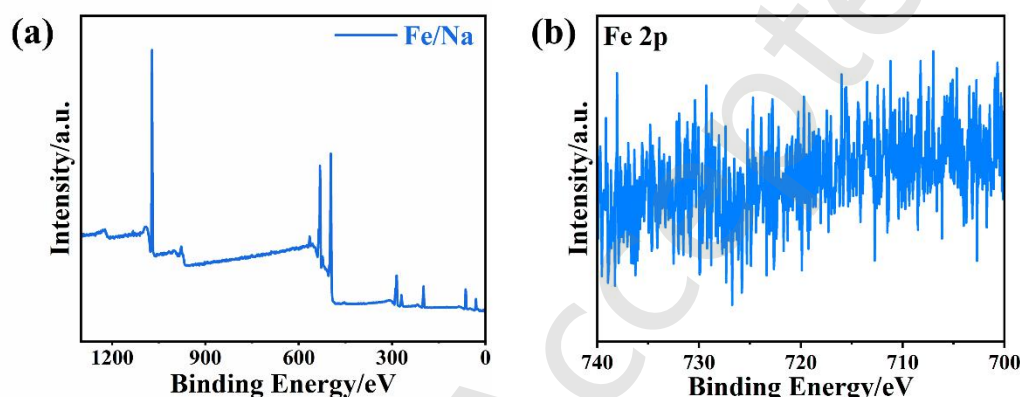


Fig. S1. XPS spectra of (a) Fe/Na and (b) Fe 2p profiles for the Fe/Na electrode, respectively.

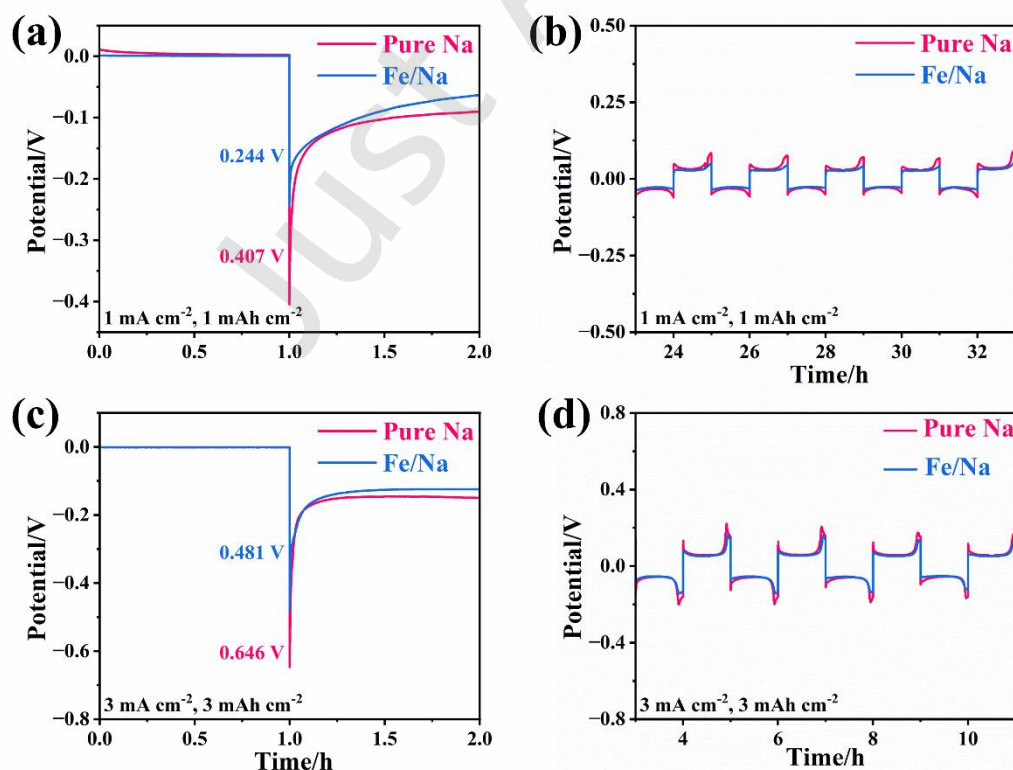


Fig. S2. Nucleation overpotential and the enlarge voltage profiles of Fe/Na||Fe/Na and Na||Na symmetric cells at 1 mA cm⁻² (a, b) and 3 mA cm⁻² (c, d).

b) and 3 mA cm^{-2} (c, d), respectively.

Table S1. Charge-transfer resistance (R_{ct}) of pure Na and Fe/Na measured at different temperatures.

T/K	pure Na R_{ct}/Ω	Fe/Na R_{ct}/Ω
298	665.27	51.8
303	395.94	45.4
308	319.59	38.7
313	269.64	29.9

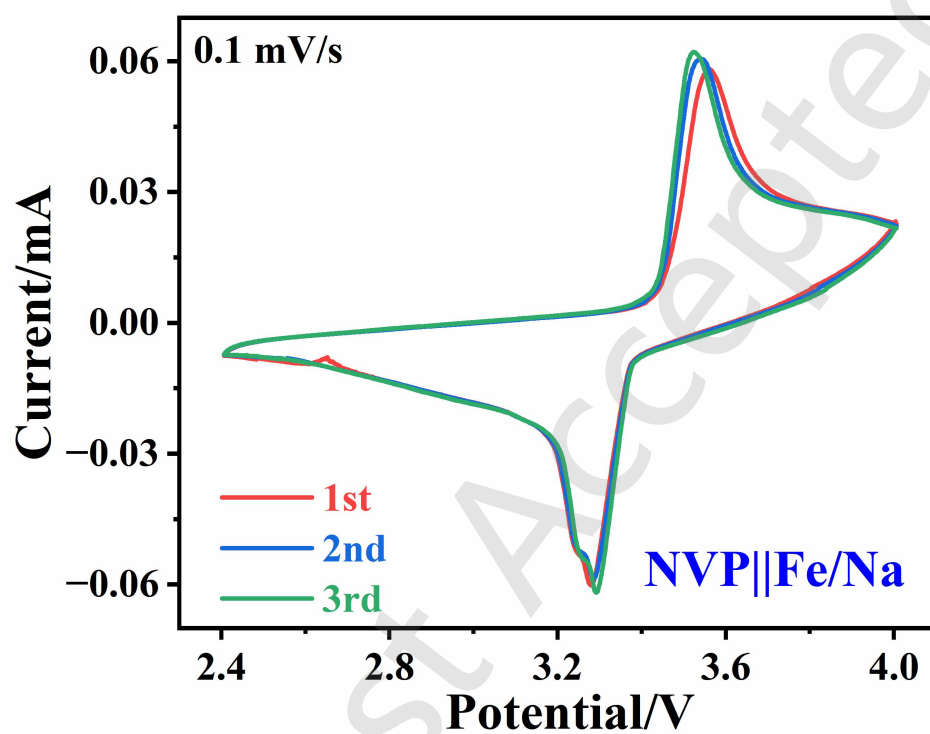


Fig. S3. CV curves of the NVP||Fe/Na full cell evaluated at 0.1 mV/s.

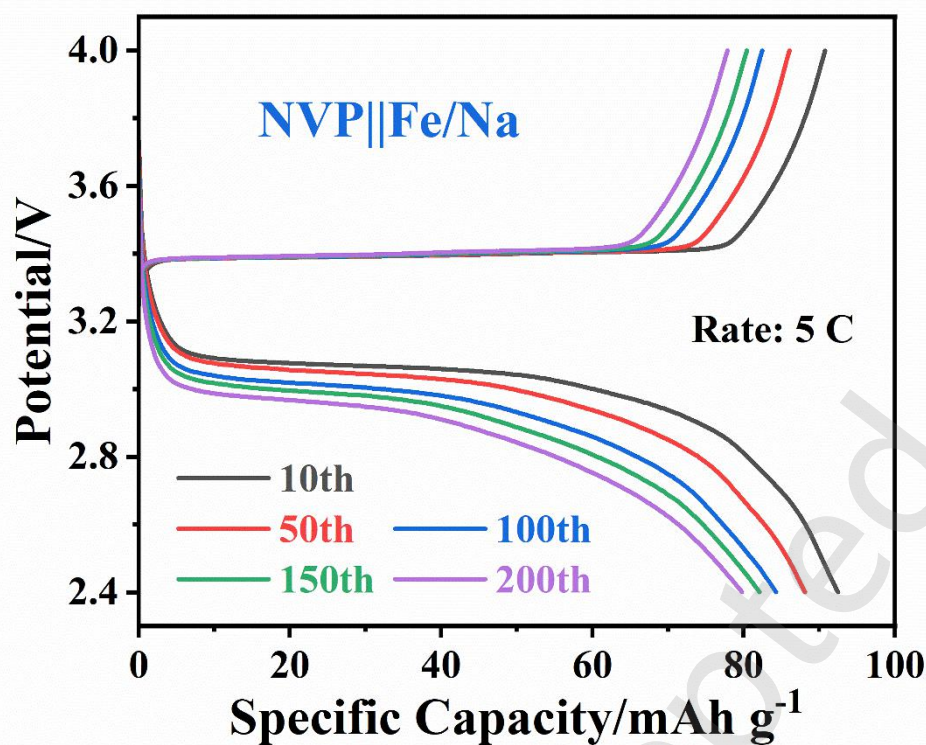


Fig. S4. Typical charge–discharge voltage profiles of the NVP||Fe/Na full cell recorded in different cycles (charged at 0.1 C, discharged at 5 C).

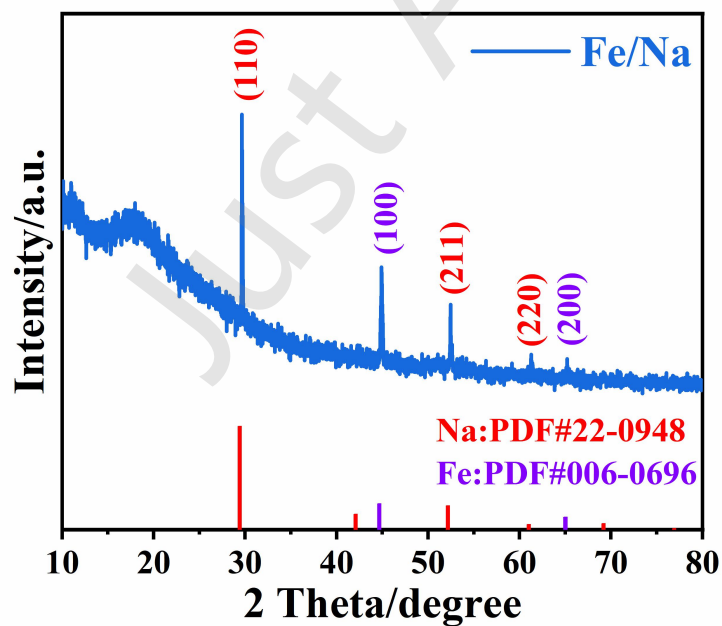


Fig. S5. *Ex-situ* XRD pattern of Fe/Na electrode after 100 cycles under the test condition of 0.1 mA cm⁻² and 0.1 mAh cm⁻².

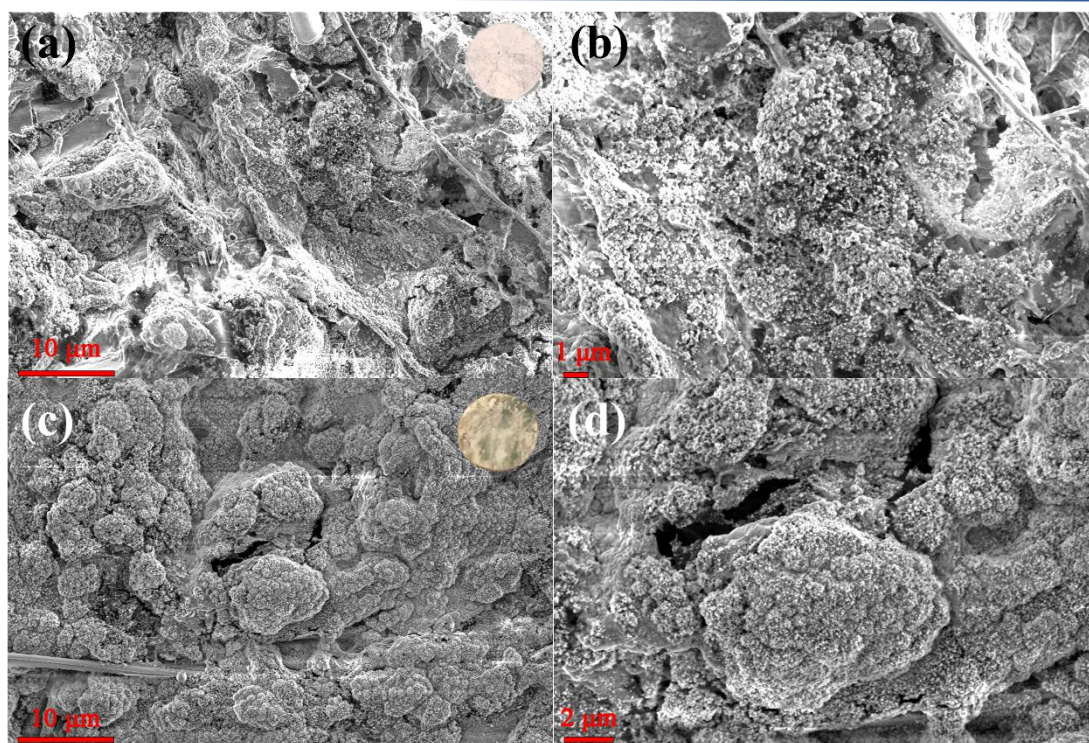


Fig. S6. SEM images of the long-term cycled (a) pure Na and (b) Fe/Na electrodes (100 times at 0.1 mA cm^{-2} and 0.1 mAh cm^{-2}).

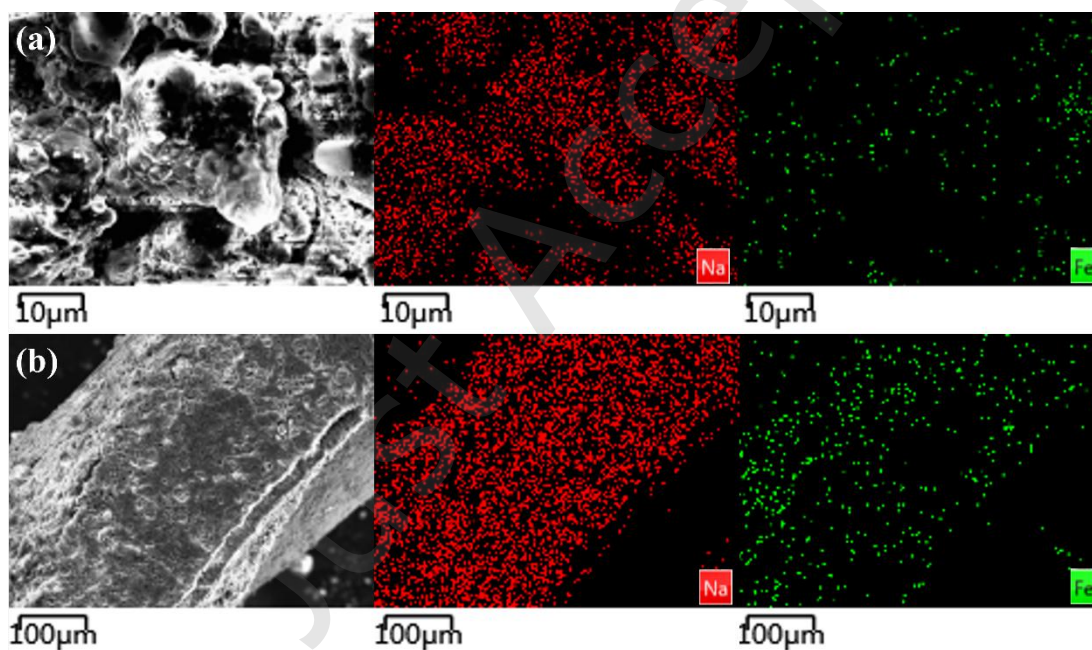


Fig. S7. The element mapping images of the surface (a) and cross section (b) of long-term cycled Fe/Na electrodes.