# Ultra-Long and Rapid Operating Sodium Metal Batteries Enabled by Multifunctional Polarizable Interface Stabilizer

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Abundant and economical sodium (Na) metal batteries promise superior energy densities compared to lithium-ion batteries; however, they face commercialization challenges owing to problematic interfacial reactions leading to dendrite formation during cycling. This paper reports the ultra-long and rapid operation of Na metal batteries enabled by the introduction of a vinylpyrrolidone (VP)-based multifunctional interface stabilizer in the electrolyte. The VP electrolyte additive provides benefits such as surface flattening, durable solid electrolyte interphase layer formation, preservation of fresh Na, and acceleration of horizontal crystal growth along the (110) plane. Symmetric Na–Na cells with the stabilizer exhibit notably stable operation for over 5 000 cycles at a high current density of 5 mA cm<sup>-2</sup>, surpassing previous research. Performance improvement is also demonstrated in a full-cell configuration with an Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>O<sub>2</sub>F cathode. This approach offers a promising solution for achieving performance levels comparable to lithium-ion batteries in Na metal battery technology.

## 1. Introduction

Lithium-ion batteries (LIBs) have dominated the energy storage market, yet the rapidly growing demand for LIBs has accelerated critical issues such as the depletion and unstable cost fluctuation of Li raw materials.<sup>[1]</sup> To address these issues, research is underway to identify charge-carrier alternatives among alkali metals for the realization of economical non-Li rechargeable batteries. Sodium (Na) stands out as a promising charge carrier candidate owing to its exceptional resource capacity, over 400 times more abundant than Li, and availability in seawater.<sup>[1b,2]</sup> Substantial research has been conducted to develop customized electrode materials for both cathodes and anodes. Considering the incompatible Na accommodation of conventional graphite anodes used in LIBs, attempts have been made to seek suitable anode alternatives, including carbon-based (e.g., hard carbon) and non-carbon-based anodes (such as Sn and Sb).<sup>[3]</sup> Nevertheless, to achieve the desired energy density threshold of 500 Wh kg<sup>-1</sup>, surpassing current LIBs,<sup>[4]</sup> advancements are needed in maximizing anode capacity and ensuring the lowest working potential for higher cell voltage.

Na metal is considered a promising anode material due to its exceptionally high theoretical capacity (approximately 1166 mAh g<sup>-1</sup>) and low electrochemical potential (–2.714 V vs the standard hydrogen electrode), thereby reaching theoretical specific energy densities of 863–1,876 Wh kg<sup>-1</sup>.<sup>[4,5]</sup> However, Na metal anodes for Na–metal batteries (NMBs) face intrinsic challenges similar to those of Li metal anodes in LIBs, which must

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/aenm.202304504

#### DOI: 10.1002/aenm.202304504

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Figure 1. Schematic depicting the Na ion plating process in Na metal electrodes with (w/) and without (w/o) the VP additive.

be addressed before commercialization. Na is highly reactive and undergoes rapid oxidation upon exposure to atmospheric conditions. When in contact with most organic electrolytes, highly reactive byproducts accumulate on the Na metal surface.<sup>[6]</sup> The formation of an unstable solid electrolyte interphase (SEI) layer during the discharge process leads to crack formation on the Na metal surface, thereby continuously forming a thick SEI layer and dead Na. The continuous consumption of the electrolyte to form an SEI layer ultimately reduces the Coulombic efficiency and battery lifespan. In addition, defect sites on Na metal can easily induce selective nucleation and subsequent preferential Na growth with a dendritic appearance. The formed Na dendrites may unexpectedly penetrate the separator and reach the opposite cathode, resulting in a short circuit and battery explosion. Therefore, effective surface reaction control of Na metal anodes is essential, including i) durable SEI layer formation and ii) the maintenance of a uniform anode surface for Na plating and stripping.<sup>[7]</sup>

Various strategies have been considered to regulate the deposition and stripping behavior of Na ions and consequently stabilize the surfaces of Na metal anodes without dendrite formation. The research approaches include i) modification of electrolyte composition, ii) introduction of stabilizing electrolyte additives, iii) engineering of artificial SEIs, and iv) construction of 3D current collector host materials for Na deposition.<sup>[8]</sup>Among these strategies, the introduction of electrolyte additives offers simple and facile benefits including adjustable functionality, easy application to existing electrolytes, SEI stabilization, and improved efficiency. The ultimate additive candidates should satisfy strict requirements to achieve i) controlled Na nucleation and lateral growth, ii) a surface flattening effect without dendrite formation, iii) durable SEI formation, and iv) reversible Na deposition and stripping; however, most additives meet only one or two requirements. Among the prominent electrolyte additives, vinylene carbonate (VC) plays a key role in enhancing the quality of SEI layer formation, whereas fluoroethylene carbonate (FEC) aids in battery stabilization by inducing uniform deposition.<sup>[9]</sup> Our previous research introduced the concept of using polarizable molecular dipole additives for long-term cycle stability in Li metal batteries. These additives offer surface-flattening effects for repeated cycling and strengthen the SEI layer using durable carbonate and fluoride species instead of weak oxide species. However, no further attempts have been made for Na metal, which is a more reactive and unstable alkali metal anode.

In this study, we report NMBs with exceptional cycle lifespan, enabling 5000 cycles at a rapid operation rate of 5 mA cm<sup>-2</sup>, achieved by introducing a vinyl pyrrolidone (VP) monomer as a polarizable molecular dipole electrolyte additive. VP molecular dipoles offer advantages such as i) uniform surface deposition of Na by their preferential adsorption on Na defect sites and ii) formation of a dense and durable SEI layer by the preferential decomposition of the VPs themselves (Figure 1). The surfaceflattening effects of the Na metal anode were elucidated by directly observing its surface morphology and measuring its surface roughness. We determined the chemical composition and atomic distribution along different depth structures to investigate the stabilization effect of the SEI layer by the VP additive. We also examined the nucleation and growth behavior of the crystalline Na phase and verified the controlled crystal arrangement of Na. To further elucidate the selective adsorption and lateral growth mechanism of Na assisted by VP molecular dipoles, changes in

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the binding energy were examined by density functional theory (DFT) calculations. Finally, we assessed the potential of VP as an ultimate molecular dipole additive by conducting Na–Na symmetric cell tests and Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>O<sub>2</sub>F/Na metal cell tests. Our study provides a feasible solution for developing NMBs with exceptionally long lifetimes and fast-cycle operations as promising alternatives for low-cost and high-energy rechargeable batteries.

### 2. Results and Discussion

## 2.1. Vinyl Pyrrolidone Molecular Additive for Stabilizing Na–Metal Batteries

We adopted a simple approach by introducing a VP-based molecular dipole additive into the electrolyte to successfully stabilize the Na metal anode for harsh and repeated cell operation. Our research aims to elucidate the various functionalities of pyrrolidone-based molecular dipole additives in NMBs, including i) suppression of dendrite formation on the Na metal anode, ii) induction of a stable and efficient SEI laver formation. iii) inhibition of byproducts from side reactions and facilitating the formation and rearrangement of Na metal crystalline structure, and iv) a comprehensive assessment of their applicability in Na metal full-cell configurations. To understand the polarity of the VP molecule, we performed calculations using Gaussian 09 and Gauss View 6.0. The characterization study of the VP molecule was carried out at the TD-SCF method in the Gaussian 09 program together with the 6-31G and using density functional theory (DFT). The dipole moment and polarizability of the VP molecules were 4.18 D and 79.525 a.u., respectively (Figure 1; Figure S1a, Supporting Information). Furthermore, the biased electrostatic potential map of the VP molecule indicates the possibility of being adsorbed onto the charged Na metal anode, affected by the accumulation of electrons under an electric field. In the absence of VP, the direct binding of Na ions to the dendrites induces a current concentration for Na plating. To summarize the advantageous reaction mechanism of the VP molecular dipole electrolyte additive in NMBs, a schematic of the Na-ion plating process with and without additives is shown in Figure 1. In the case of a pristine electrode that does not incorporate the VP additive during the charging process, the deposition of Na ions onto the Na metal anode induces the formation of dendrites. After continuous cycling, this leads to volumetric changes in the anode and the induction of porous Na metal, along with the formation of a thick and unstable SEI layer and capacity degradation owing to the occurrence of dead Na. Furthermore, if the grown dendrites reach the opposite electrode by penetrating the separator, it can result in a hard short circuit.<sup>[10]</sup> However, when stabilization is included using molecular dipoles during the deposition and stripping processes, even after continuous charge-discharge cycles, a thin and uniform SEI layer is formed, effectively eliminating the risk associated with dendrites.

#### 2.2. Morphological Surface Flattening Effect of Vinyl Pyrrolidone Electrolyte Additives

To verify the dendrite suppression and surface leveling effects of VP molecular dipole additive on the Na metal anode, we conducted ex situ scanning electron microscopy (SEM) characterization of the Na metal anodes collected after 20 cycles under a current density of 1 mA cm<sup>-2</sup>. Without VP, severe cracking was observed over the entire surface of the Na metal anode (Figure 2a; S2a, Supporting Information). The observation indicates that the formed SEI layer on the surface could not be stably maintained during continuous charge and discharge cycles. As the SEI layer deteriorates, the reactive Na metal is continuously exposed inside the cracked SEI layers, resulting in unwanted continuous SEI layer formation and irregular Na deposition. In contrast, a smooth surface was maintained without significant cracks by including the VP molecular dipoles (Figure 2b; Figure S2b, Supporting Information). Viewed along the vertical direction, the Na metal anode cycled without VP exhibited separated Na deposition layers, which were relatively porous (Figure 2c). Conversely, a dense Na deposition layer was formed using the VP-containing electrolyte (Figure 2d). Energy dispersive X-ray spectroscopy (EDS) mapping results indicate the morphological uniformity and thickness of the formed Na deposition layers (Figure 2e). In the absence of the VP additive, porous layer features were found owing to weak Na deposition layer coherence, corresponding to the vertical SEM observation. In contrast, when the VP additive was included, a dense and uniform Na deposition layer was formed without split features between the layers (Figure 2f). Atomic force microscopy (AFM) measurements were performed in an Ar-filled glove box to examine the surface roughness and height of the Na metal anode surface at the microscopic scale after 100 cycles with and without VP (Figure 2g-i). Compared to the rough and nonuniform surface morphology of the Na metal cycled without VP, greater uniform surface roughness and cross-sectional height uniformity were achieved through VP addition (Figure 2g,h). Specifically, a high degree of surface roughness (38.027 nm) was observed for the Na metal anode cycled without VP, whereas a significantly lower surface roughness (1.699 nm) was achieved through VP addition. By comparing the cross-sectional height fluctuation data, we confirmed that the VP molecules contributed to the enhancement of a smoother surface without significant height deviations for the Na metal electrodes (Figure 2i).

#### 2.3. Strengthening the Chemical Composition of the SEI Layer

Another benefit of the VP molecular dipole is that, in addition to the surface flattening effect, the VP additive can participate in the SEI layer as a result of self-reduction and as an electrolyte species. We compared the energy levels of diethylene glycol dimethyl ether (DEGDME) as a solvent and the VP molecular dipoles obtained from the calculations. The VP added to the DEGDME electrolyte had a lower LUMO energy than the electrolyte solvent. This result implies that the VP additive is more reductive than the DEGDME electrolyte, thereby decomposing first, suppressing solvent decomposition during battery operation, and prioritizing the formation of the SEI layer during the first cycle.<sup>[11]</sup> To examine the chemical components of the SEI layer, ex situ surface analysis of the Na metal anodes collected at different cycles (1st, 20th, and 100th cycles) with and without the VP molecular dipole additive was conducted using Xray photoelectron spectroscopy (XPS). To conduct an in-depth

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**Figure 2.** Ex situ surface morphology of Na–Na symmetric cell observed at a current density of 1 mA cm<sup>-2</sup>. SEM images of Na metal electrodes after 20 cycles in electrolyte with and without VP: a) top view using an electrolyte without VP and b) with VP, and c) side view using an electrolyte without VP and d) with VP. EDS mapping images of the cross-section of the Na metal electrode: e) without VP and f) with VP. AFM images of the Na metal electrode after 100 cycles at a current density of 5 mA cm<sup>-2</sup>: g) without VP, h) with VP, and i) cross-sectional height comparison for both conditions.

analysis of the uneven metal anode surface confirmed through the previous SEM and AFM results, the depth profiles of the SEI layer are shown in Figure 3a-h. Analysis of the composition formed with depth after the first cycle and after the 20th cycle revealed a distinct difference in the composition between the surface and internal layers (Figure 3a,b,e,f). During the chargedischarge process, a thin and dense SEI layer is predominantly formed on the surface. The chemical composition of the SEI surface formed after the first cycle and beyond the 20th cycle depended on the presence of the additive (Figure S3, Supporting Information). While the dominant components were similar to each other, a difference in the ratio of NaF (685.7 eV) and ionic C-F (683.9 eV) components was observed. According to previous studies, C-F bonds can be categorized as covalent C-F bonds (sp<sup>3</sup> orbitals), semi-ionic C-F bonds (sp<sup>2</sup> hybridized orbitals), and ionic C-F bonds.<sup>[12]</sup> During the cycling process, a thermodynamically spontaneous reaction occurred between Na and the C-F components of the SEI layer.<sup>[13]</sup> Therefore, the existence of dominant ionic C-F bonds with the weakest bonding strength among the C-F bonds suggests the possibility of inducing a NaF-rich SEI layer (Figure S3, Supporting Information).<sup>[14]</sup> Furthermore, by collecting the XPS profiles of the deeper part, the Na metal anode cycled with VP showed an increase in the NaF content from the ionic C-F, resulting in the formation of a NaF-rich SEI layer, in contrast to the NaPF<sub>6</sub> salt signal for Na anodes cycled without VP (Figures S4c,g and S5c, Supporting Information). Furthermore, a higher Na metal signal in the case of VP addition was confirmed at greater depths compared to Na metals cycled without VP (Figure S4d,h, Supporting Information). This result verifies that a significant amount of fresh Na was successfully retained. We further analyzed the elemental composition at different depths after the 100th

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**Figure 3.** Ex situ analysis of the SEI layer composition on Na metal anodes. Atomic percentages of O, C, F, and Na by XPS depth profiling after a) 1st cycle, b) 20th cycle, and c) 100th cycle when electrolyte without VP was used, and after e) 1st cycle, f) 20th cycle, and g) 100th cycle when electrolyte without VP was used. Graphs showing atomic percentages of Na by cycle number: d) without VP and h) with VP. 3D TOF-SIMS intensity variation for Na-metal electrodes, showing spatial distributions of selected ions: i) <sup>18</sup>O<sup>-</sup>, j) C<sup>-</sup>, k) F<sub>2</sub><sup>-</sup>, and l) Na<sup>-</sup> without VP and m) <sup>18</sup>O<sup>-</sup>, n) C<sup>-</sup>, o) F<sub>2</sub><sup>-</sup>, and p) Na<sup>-</sup> with VP.

cycle. After 100 cycles, it is evident that the SEI layer became considerably thicker than that with fewer cycles. In the case where VP additives are not included, it can be observed that the proportion of Na components within the interior has significantly decreased, reaching  $\approx$ 30% after 100 cycles. However, when VP additives were included, even after 100 cycles, the interior still contained a higher proportion of Na components, exceeding 50%, verifying stable preservation of fresh Na metal (Figure 3c,d,g,h). The depth analysis results for C 1s, O 1s, F 1s, and Li 1s further confirm that the introduction of VP has resulted in the formation of durable SEI layers enriched with NaF and ionic C—F (Figures S4 and S5, Supporting Information). Using the VP molecular dipole additive, stronger

Na peaks appeared under a thin fluoride-rich layer of the SEI layer.

To further elucidate the detailed chemical species in the SEI layer formed by adding VP, a time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis was conducted (Figure 3i–p; Figure S6, Supporting Information). We gathered geometric chemical information regarding the 3D distribution of the organic and inorganic components in the formed SEI layer. It was observed that <sup>18</sup>O<sup>-</sup> is uniformly present throughout the SEI layer, regardless of the presence of VP molecules, a typical result of electrolyte decomposition. The amount of the C<sup>-</sup> component in the surface layer decreased in the case of Na metal cycled without VP (Figure S6, Supporting Information). In contrast, the

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Figure 4. Ex situ XRD patterns of Na metal anode with and without VP at different cycle numbers. XRD of Na metal after a) 10th plating and b) 50th plating for the two electrolyte conditions. Illustrations of four different Na surfaces: c) (100), d) (110), e) (211), and f) (210). g) Binding energies of Na (green) and VP (gray) across different Na surfaces and binding sites.

C<sup>-</sup> content was maintained at depth for the Na metal cycled with VP. The maintenance of the C<sup>-</sup> signal along the deep side of the Na metal cycled with VP implied a higher and deeper portion of durable carbonate components in the SEI layer. Compared to the Na metal cycled without VP, a higher proportion of  $F_2^-$  species were detected on the surface of the SEI layer for Na metals cycled with VP, aligning with the XPS data. The presence of VP in the electrolyte led to a richer induction of fluorine components in the SEI layer. For Na<sup>-</sup>, in the case of the Na metal anode cycled without VP, irregular fluctuations in intensity were observed with depth. However, when the VP additives were included, a uniform and deeper enhancement in the proportion of the Na components was observed. These results also suggest ample fresh Na metal within the interior and a dense, uniform formation of the SEI layer, as supported by ex situ XPS results (Figure 3i-p; Figure S6, Supporting Information). From the ex situ XPS and TOF-SIMS analysis, we conclude that the introduction of VP molecular dipole additives offers bifunctional advantages including i) the formation of durable fluoride and a carbonaterich SEI layer and ii) maintenance of higher fresh Na metal contents.

# 2.4. Crystallinity Growth Rearrangement Effect of Vinyl Pyrrolidone Molecular Additive

To examine the crystal structural changes of the Na metal anode after cycling with and without VP, ex situ X-ray diffraction (XRD) analysis was conducted (Figure 4a,b; Figure S7, Supporting Information). After the 1st charge, the (110) plane, which induces reversible deposition and stripping without the formation of dead Na,<sup>[13]</sup> was prominently formed on the Na metal anode, verifying the crystalline rearrangement of the Na metal anode (Figure S7, Supporting Information). Ex situ XRD measurements were conducted on the Na metal anode after longer cycles (10 and 50 cycles) to confirm whether crystal rearrangement continued with cycling (Figure 4a,b). After 10 cycles, for the Na metal cycled without VP additives, the crystallinity of fresh Na almost disappeared owing to severe side reactions with the electrolyte originating from thick SEI formation during repeated cycling. In contrast, a strong intensity in the (110) plane was observed when VP additives were introduced. This suggests that the rearrangement of crystallinity toward the (110) plane was maintained by the addition of VP. After 50 cycles, when an electrolyte

without VP additives was used, no peaks indicating the crystallinity of the Na metal were observed, and peaks corresponding to the sodium oxide phase appeared, which resulted from the accumulation of unwanted side-reaction products. Conversely, for the Na metal anode cycled with VP, consistent with previous results, the XRD peak related to the (110) plane was maintained even after 50 cycles. In addition, a negligible peak was observed for sodium oxide as a side reaction product. The ex situ XRD results demonstrate that VP molecular dipoles can i) rearrange the crystalline structure of Na metal anodes along the lateral direction, ii) stably maintain the rearranged crystal structure of Na metal anodes after repeated cycling, and iii) effectively prevent the undesired formation of side products (Figure 4a,b).

To validate our experimental findings, the binding energies of Na and VP at various binding sites and surfaces were calculated. We hypothesized that the difference in the binding energies of Na and VP would eventually influence the surface conditions of Na during battery operation. Repeated Na deposition (reduction) and stripping (oxidation) cycles tend to create rough Na surfaces. The low-coordination surface sites attract more Na atoms and act as seeds for dendrite formation. On surfaces with steps, such as the Na (210) surface, three binding sites are anticipated: convex, concave, and terrace. Because the (100) and (110) surfaces are clean and flat (Figure 4c,d), only the terrace site can be considered as a nucleation site for Na deposition. Although the terrace of the (211) surface was too shallow to differentiate the binding sites, the (210) surface of Na was ideal for exploring the different binding sites (Figure 4e,f). Therefore, we report the strongest binding energies on the (100), (110), and (211) surfaces and separate binding energies at different binding sites on the (210) surface to understand the effects of the surface indices and binding sites

Figure 4g shows the binding energies of Na (green) and VP (gray). Regardless of the surface or binding site, VP consistently exhibited stronger binding energies than Na at different binding sites. This suggests that the VP additives cover all Na-defective nucleation sites without competition. Specifically, the VP initially covered the convex site originating from low-coordination atom configurations and then extended to the terrace and concave sites. We propose that an appropriate concentration of VP will selectively cover the defect (or convex) sites, leaving the terrace and concave sites accessible to incoming Na cations, thus maintaining a flat Na surface. Through DFT calculations, we explored various surfaces ((100), (110), (211), and (210)) and binding sites (convex, concave, and terrace) to elucidate the leveling effect of the VP additives. Our calculations revealed that VP preferentially covers the defect sites on the Na surface before the arrival of Na cations, as indicated by our binding energy calculations. We believe that the unique reaction mechanism of VP maintains the Na surface as clean and flat as possible, which is consistent with our experimental conclusions.

## 2.5. Vinyl Pyrrolidone Electrolyte Additive for Electrochemical Performance Enhancement

A site-formation process is required to facilitate the flattened deposition of Na. Subsequently, Na growth occurred around these sites, and uniform deposition progressed. The overpotential occurring during site formation is referred to as the nucleation overpotential and reflects the sodiophilicity of the entire electrode surface.<sup>[15]</sup> Notably, a reduction in the nucleation overpotential due to the VP additive was clearly observed at different current densities. Figures 5a-c and S8a-c (Supporting Information) provide more detail on the nucleation overpotential at various current densities. Specifically, at a current density of 0.5 mA cm<sup>-2</sup>, deposition exhibited nucleation overpotential values of 9.79 mV without VP and 4.72 mV with VP. At a current density of 1 mA cm<sup>-2</sup>, the values were 32.99 mV without VP and 18.02 mV with VP. Under higher current density conditions of 2 mA cm<sup>-2</sup>, a higher nucleation overpotential value was observed (50.76 mV) for the cell without VP compared to the cell with VP (34.22 mV). These results demonstrate that the VP additives can effectively lower the nucleation energy barrier in the Na deposition process, resulting in smooth and uniform Na deposition. The surface morphology of the deposited Cu foil was observed using SEM (Figure S9, Supporting Information). The SEM observation reveals smooth and uniform surface formation during deposition when the VP additive is included, compared to the uneven and irregular Na deposition features on the Cu foil without VP.

We confirmed the improved cycling performance of a Na-Na symmetric cell by introducing the polarizable VP molecular dipole, offering a surface-flattening effect and a durable SEI interface to enable long and rapid cycling operation (Figure 5d). To emphasize the exceptional benefit of the additives, the Na-Na symmetric cell test was conducted under a high current density condition of 5 mA cm<sup>-2</sup>, corresponding to fast charging and discharging, identified as an extremely harsh operating condition. When the electrolyte without the VP additive was used, there was a pronounced and unstable voltage fluctuation, even in the early cycling stages (Figure S10a, Supporting Information). Notably, the cell without the additive exhibits lower overpotential at  $\approx$ 120 h (Figure S10b, Supporting Information). This phenomenon is attributed to the formation of soft short circuits caused by recoverable dendrites rather than the stabilization of the cell, leading to a voltage decrease.<sup>[16]</sup> After 374 h, a sudden voltage drop is evident, indicating the apparent occurrence of a hard short-circuit when the grown dendrites penetrate the separator and reach the opposite electrode Figure S10c, Supporting Information).<sup>[17]</sup> Conversely, for the symmetric Na-Na cell with VP, notably stable operation without significant overpotential or voltage fluctuations was achieved during 2000 h of cycling (Figure 5d). Figure 5e illustrates the average charge voltage of the symmetric cell as a function of the cycle number. Without VP, problematic voltage fluctuations occurred throughout the early stages of cycling, and a consequent short circuit occurred before 940 cycles. However, with VP, stable performance was observed over an exceptional 5000 cycles, even at a high current density of 5 mAh cm<sup>-2</sup>. We conducted a Na-Na symmetric cell test under even more severe conditions to verify the beneficial effect of VP (Figure S11, Supporting Information), doubling the current density to 10 mA cm<sup>-2</sup> at the capacity limit of 1 mAh cm<sup>-2</sup>. Although severe voltage fluctuations and poor cycle performance (73 h, 365 cycles) were observed for the cell without VP, stable operation was achieved for a significantly longer duration with VP (200 h, 1000 cycles), without a significant overpotential or short circuit. Figure 5f displays the results

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**Figure 5.** Nucleation overpotential at different current densities of a)  $0.5 \text{ mA cm}^{-2}$  and b)  $2 \text{ mA cm}^{-2}$ , and c) comparison of nucleation overpotential energies during Cu–Na deposition processes. Na–Na symmetric cell tests using an electrolyte with and without VP: d) cycling performance of the Na metal anode at 5 mA cm<sup>-2</sup> illustrated through charge–discharge curves and e) average charge voltage. f) Comparative graph of cycle performance for the Na–Na symmetric cell test reported using an ether-based electrolyte. Electrochemical performance comparison of NVPOF-Na metal cells without and with VP additive at 20 mAh g<sup>-1</sup>: g) Tafel plots of the symmetric cell without and with VP; h) selected charge–discharge curves of the 1st and 50th cycles of the NVPOF/Na metal cells without and with VP; i) charge-discharge profiles of NVPOF/Na metal with VP additive at 1st, 10th, 50th, and 100th cycles; j) cycling stability profiles of the NVPOF/Na metal electrode without and with VP.

of the electrochemical test using the Na–Na symmetric cell compared to previous studies utilizing ether-based electrolytes,<sup>[1b,18]</sup> highlighting the superior cycling performance of 5000 cycles under rapid operation conditions (5 mA cm<sup>-2</sup>) in NMBs employing the VP additive. Figure 5g presents the results of the Tafel plot analysis conducted using the Na–Na symmetric cell. A Tafel plot test was performed to assess the charge transfer kinetics, which allowed for a comparison of exchange current densities through the Tafel extrapolation method.<sup>[19]</sup> The exchange current density (0.649 mA cm<sup>-2</sup>) is significantly lower for the cell without VP compared to the cell with VP (3.157 mA cm<sup>-2</sup>), indicating that VP effectively enhanced the charge transfer kinetics and facilitated stable cycling operation. The addition of VP to a Na–Na symmetric cell significantly improved its cycling performance, enabling stable operation. This contrasts with the non-VP cell, which experienced voltage fluctuations and short-circuiting. The

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improvement is attributed to the surface-flattening and interfacial stabilization effects of VP.

To investigate whether the stabilizing effect of VP on the Na metal anode applies to practical cells beyond the Na-Na symmetric cell, we conducted NVPOF-Na metal cell tests using  $Na_3V_2(PO_4)_2O_2F$  (NVPOF) as the cathode and Na metal as the anode under different electrolyte conditions with and without VP. The reversible insertion and extraction of two Na ions were observed at a potential of  $\approx$ 3.6 (Na<sup>1</sup>) and  $\approx$ 4.0 V (Na<sup>2</sup>) versus Na<sup>+</sup>/Na in the NVPOF. (Figure S12, Supporting Information) The NVPOF/Na metal cell demonstrated improved specific capacity after the introduction of the VP additive, as shown in Figure 5h, which depicts the charge–discharge curves of the cells. In the absence of the additive, the first charge and discharge capacities were 134 and 103 mAh g<sup>-1</sup>, respectively. With the additive, the first charge and discharge capacities were 192 and 106 mAh g<sup>-1</sup>, respectively, resulting in an additional 58 mAh g<sup>-1</sup> of initial charge-specific capacity. This additional capacity for the first charge is attributed to the oxidation reaction of VP during the charging process, suggesting that VP acts as a sacrificial additive to form durable fluoride and carbonate SEI layer species on the Na surface.<sup>[20]</sup> Nevertheless, Figure 5i shows consistent charge-discharge curve features for the 1st, 10th, 50th, and 100th cycles except for the first charge reaction. The cycling performance of NVPOF/Na metal electrodes with and without the VP additive was tested at a current density of 20 mA  $g^{-1}$  (Figure 5j). Throughout the 100 cycles, it can be observed that the capacity continuously degrades in the case of the NVPOF-Na metal cell without VP. In contrast, when VP was introduced into the electrolyte, no significant degradation was observed over 100 cycles. This suggests that the beneficial effects of the VP additives extend to NVPOF-Na metal cells without inducing side reactions or degradation behavior with NVPOF cathodes.

### 3. Conclusion

In summary, we introduced a VP molecular dipole electrolyte additive as a multifunctional interface stabilizer to achieve ultralong and rapid operation of NMBs. The VP-based interface stabilizer offers several advantages, including i) uniform and flattened surface deposition of Na, ii) formation of a dense and durable SEI layer with fluoride and carbonate species, iii) preservation of fresh Na internally, and iv) acceleration of horizontal crystal growth along the (110) plane. We confirmed the flattened surface morphologies of the Na metal with a thin and uniform SEI layer by adding VP. Ex situ surface characterization results demonstrated the formation of a durable fluoride- and carbonate-rich SEI layer with preservation of the fresh Na metal, which was facilitated by VP's role in functionally regulating electrolyte decomposition. Crystalline rearrangement of the Na metal anode along the lateral direction assisted by VP was also demonstrated without the formation of sodium oxide side products. The binding characteristics of Na and VPs on the defect sites were also analyzed using DFT calculations. Finally, we achieved superior cycle performance in Na–Na symmetric cells (> 5000 cycles at 5 mA cm<sup>-2</sup>) and NVPOF/Na metal cells using the molecular dipole interface stabilizer in the electrolyte. This study provides useful guidelines for developing various functional electrolyte additives to ensure the long-term stability and safety of NMBs.

## 4. Experimental Section

Preparation of Electrolyte with VP: N-vinylpyrrolidone (VP, 99%) was added to 1  $\bowtie$  NaPF<sub>6</sub> in diethylene glycol dimethyl ether (DEGDME) (Well-cos Corp.) to prepare the electrolyte with VP. The concentration was adjusted to 1 wt.% and stirred at room temperature for 24 h. All the materials were purchased from Sigma-Aldrich (Korea). All handling and operation steps were performed in an Ar-filled glove box (H<sub>2</sub>O and O<sub>2</sub> < 0.1 ppm).

Preparation of the Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>O<sub>2</sub>F (NVPOF) Cathode: Carbon-free Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>O<sub>2</sub>F (NVPOF) was hydrothermally synthesized under precise pH control. Vanadium oxide ( $V_2O_5$ , 98%) and oxalic acid ( $H_2C_2O_4$ , 98%) (molar ratio: 1:3) were dissolved in distilled (DI) water and stirred for 1 h at 70 °C. Next, stoichiometric ammonium phosphate monobasic (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, 99%; JUNSEI) and sodium fluoride (NaF, 99.99%) were added to the solution under continued stirring. Ammonium hydroxide solution (NH<sub>4</sub>OH) was used in the final solution to adjust the pH of the solution to 7.0. Subsequent heating and stirring were simultaneously performed at 170 °C for 12 h using a high-pressure reactor (HR-8200; Hanwoul Engineering Co., Ltd.), followed by natural cooling. The light blue precipitate of NVPOF was washed several times with DI water, and dried in a vacuum oven at 80 °C.<sup>[20]</sup> The cathode was prepared by mixing the active material (70 wt.%), acetylene black (AB) (20 wt.%), and poly(acrylic acid) (PAA) binder (5 wt.%; average Mw  $\approx$ 450 000) dissolved in DI water (10 wt.%). The slurry was uniformly cast on carbon-coated Al foil and vacuum-dried at 70 °C for 12 h.

*Na–Na Symmetric Cell Tests*: Na–Na symmetric cells were assembled using R2032 coin-type cells (Wellcos Corp.) in an Ar-filled glove box. A 12mm diameter Na metal foil was used for both electrodes, and Celgard 2500 polypropylene (PP) was used as the separator. The electrolyte comprised 1  $\bowtie$  NaPF<sub>6</sub> in DEGDME (Wellcos Corp.), with and without 1 wt.% VP.

NVPOF-Na Metal Cell Tests: Cell tests using a Na metal anode (Ø 12 mm) and NVPOF cathode (Ø 14 mm) were constructed. The base electrolyte was 1 M NaPF<sub>6</sub> in DEGDME and two types were tested: one including the VP additive and the other without it. Glass microfiber filters (Whatman GF/A microfiber filter paper) and anodic aluminum oxide (AAO) were used as separators. All cells were cycled in the voltage range of 2.0 V  $\leq$  U  $\leq$  4.3 V versus Na/Na<sup>+</sup>.

*Electrochemical Measurements*: All electrochemical analyses were performed at room temperature. Charge–discharge cycle tests using Na–Na symmetric cells and NVPOF/Na metal cells were conducted using a battery cycler (WBCS3000S battery test system, WonATech).

*Ex-Situ Characterization*: Surface morphologies were observed using field-emission scanning electron microscopy (FE-SEM, JSM-7600F, JEOL) at an accelerating voltage of 5 keV. Elemental analysis was performed using EDS with SEM. The surface roughness was investigated using AFM (NX-10, Park Systems, Korea) in a glove box. The surface and depth atomic compositions of the Na metal electrodes after cycling were investigated using XPS (NEXSA, Thermo Fisher Scientific). TOF-SIMS was conducted on a TOF.SIMS5 instrument (ION-TOF, Münster, Germany), and negative polarity data were collected using a 30 keV Bi<sup>3+</sup> ion source. The area of analysis was 100 × 100 µm. Depth profiles were obtained by sputtering ion beams of Cs<sup>+</sup> (3 keV) on a 300 × 300 µm square. The sputtering rate was 300 µm. The crystal structure of the Li metal electrode was characterized using XRD (D8 Advance, Bruker) with Cu-Ka ( $\lambda = 1.54$  Å).

*Computational Details*: Vienna ab initio simulation package (VASP) was used for the calculations. The generalized gradient approximation (GGA)-based revised Perdew-Burke-Ernzerhof (RPBE) functional<sup>[21]</sup> was employed to consider electron exchange and correlation, which is known to be suitable for surface chemistry research. The cutoff energy was set to 400 eV, and the Brillouin zone was sampled at  $2 \times 2 \times 1$  based on the Monkhorst-Pack scheme. The convergence criteria for the electronic and geometric optimizations were  $10^{-5}$  eV and  $10^{-2}$  eV Å<sup>-1</sup>, respectively.

Four different Na surfaces, (100), (110), (211), and (210), were modeled to investigate the influence of the VP additives during battery cycling. These surfaces were selected based on the XRD analysis. In the previous study, a Li (110) surface was used with steps;<sup>[8d]</sup> however, considering multiple surfaces provides more accurate conclusions. The surfaces were categorized into two groups: flat ((100) and (110)) and stepped ((211) and (210)). Both the (211) and (210) surfaces were derived from the (110) surface through different step configurations. The surface models were centered in a 20 Å vacuum layer along the z-direction. The following equation was used to calculate the binding energies of the Na and VP additives:

$$\Delta E_{\text{bind.}} = \Delta E_{\text{Na slab+VP}} - \Delta E_{\text{Na slab}} - \Delta E_{\text{VP}}$$
(1)

Here,  $\Delta E_{\rm bind.}$  is the binding energy of the adsorbate (Na or VP additives),  $\Delta E_{\rm Na\ slab} + {\rm VP}$  is the total energy of the system after adsorbate binding,  $\Delta E_{\rm Na\ slab}$  is the total energy of the Na slab, and  $\Delta E_{\rm VP}$  is the cohesive energy of Na or gas energy of VP additives.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

#### Acknowledgements

This study was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean Government (MSIT) (No. RS-2024-00404414). This study was supported by the KIST Institutional Program (Project No. 2E31861).

### **Conflict of Interest**

The authors declare no conflict of interest.

## **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

dendrite suppression, multifunctional electrolyte additive, Na-metal batteries, N-vinylpyrrolidone, surface leveler

> Received: December 26, 2023 Revised: June 4, 2024 Published online: July 3, 2024

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