COMPARATIVE EVALUATION OF ANODE-FREE SODIUM METAL CELLS

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Sodium metal batteries are attracting attention as sustainable alternatives for next-generation energy storage due to their abundance and cost-effectiveness. The anode-free sodium cell configuration simplifies design, cuts costs, and may boost energy density. In this study, we evaluated the electrochemical performance of anode-free sodium metal cells using two distinct electrolyte compositions. The cells showed stable cycling, lasting over 2000 cycles at 1.5 mA/cm² with about 99.99% Coulombic efficiency. Our findings highlight the importance of electrolyte choice in enhancing plating and stripping processes and demonstrate the potential of anode-free sodium cells as efficient, economical, and sustainable energy solutions.

Keywords: sodium-metal cell, anode-free configuration, cycles, Coulombic Efficiency

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1. Introduction

The integration of renewable energy sources into the global power grid is crucial for reducing reliance on fossil fuels and mitigating the environmental impact associated with their usage. However, the inherently intermittent and geographically uneven nature of renewable energy sources such as solar and wind poses significant challenges for consistent energy supply and distribution. Consequently, efficient, scalable, and economically viable energy storage technologies have become critical for balancing energy production and consumption, thus enabling a stable and reliable renewable energy grid integration [1]. While lithium-ion batteries (LIBs) currently dominate commercial energy storage markets owing to their maturity, high energy density, and extensive research and development, their widespread adoption is hampered by the uneven geographical distribution, limited availability, high extraction costs, and environmental concerns associated with critical raw materials such as lithium, cobalt, and nickel [2–6].

Sodium-ion batteries (SIBs) are increasingly recognized as a promising alternative to LIBs, particularly for large-scale, stationary energy storage applications. SIBs leverage sodium's abundant availability in the Earth's crust, uniform geographic distribution, and significantly lower cost compared to lithium-based materials, enabling broader scalability and alleviating supply chain constraints. Moreover, the working principles and manufacturing processes of SIBs closely resemble those of LIBs, facilitating their rapid transition into existing battery production infrastructure. Recent advancements in electrode materials, electrolyte formulations, and cell engineering have further improved the electrochemical performance of SIBs, enhancing their stability, cycling efficiency, and overall practicality [7–10]. Despite these promising developments, achieving energy densities and cycle life comparable to or surpassing those of lithium-based systems remains a critical research objective.

In recent years, anode-free battery designs have emerged as a highly innovative configuration to enhance battery energy density by eliminating traditional anode host materials. In lithium-based battery systems, the anode-free approach effectively employs a fully lithiated cathode coupled with a bare current collector, significantly improving gravimetric and volumetric energy densities by avoiding excess active material. Extending this concept to sodium systems, anode-free sodium metal batteries (AFSBs) utilize direct sodium plating onto bare current collectors during initial charge cycles, thereby capitalizing on the high theoretical specific capacity of sodium metal (1166 mAh/g, which is more than double that of common anode materials such as sodium–tin alloys, e.g., $Na_{15}Sn_4$) and its low reduction potential. Furthermore, the low density of sodium metal (0.97 g/cm³) inherently supports high volumetric and areal capacities without the

necessity of complex electrode architectures or diffusion-limiting host materials. These advantages position AFSBs as a promising, cost-effective, and high-performance solution for next-generation electrochemical energy storage.

However, significant hurdles remain in the practical implementation of anode-free sodium metal cells. Challenges include limited Coulombic efficiency (CE), insufficient cycle life, dendrite formation, and incomplete understanding and optimization of the solid-electrolyte interphase (SEI). Indeed, sodium metal exhibits lower electrochemical stability and is notably more reactive than lithium metal with common electrolyte solvents, particularly carbonate-based electrolytes, complicating SEI formation and stability [11].

Addressing these issues requires substantial research into advanced electrolyte chemistries, surface engineering techniques, and improved cell design strategies.

With this motivation, the present study systematically investigates the feasibility and performance of anode-free sodium metal cells, focusing on the critical role played by electrolyte composition on the Na-metal plating/stripping efficiency. Specifically, we provide a comparative evaluation of two promising electrolyte formulations (1M $NaCF_3SO_3$ - sodium trifluoromethanesulfonate and 1M $NaPF_6$ - sodium hexafluorophosphate, dissolved in diglyme solvent) in an anode-free sodium cell configuration. Our work aims to clarify how electrolyte choice influences long-term cycling stability, CE, and overall electrochemical performance, thus contributing vital insights to advance practical applications of sustainable sodium-based battery technologies.

2. Experimental section

All materials used in this study were of analytical grade and were employed without further purification. CR2032 316-grade stainless steel cases were sourced from TOB NEW ENERGY TECHNOLOGY CO., LTD. The electrolyte salts, including sodium trifluoromethanesulfonate ($NaCF_3SO_3$) and sodium hexafluorophosphate ($NaPF_6$), were also obtained from the same manufacturer, and used as received. The ether-based solvent used in the electrolyte, Diglyme (G2), was purchased from Sigma-Aldrich. The Celgard 2325 separator was supplied by Celgard, sodium metal electrodes were acquired from AOT Electronics Technology, and the copper foil (14 μm thickness) for the current collector was provided by MTI Corporation.

By utilizing the anode-free cell architecture, a bare copper foil current collector electrode, and a simple sacrificial sodium source, we successfully demonstrated the viability of this approach. This methodology resulted in achieving, in some cases, over 2000 cycles at a current density of 1.5 mA/cm² within a coin cell configuration. Our investigation used a copper current collector

substrate in combination with different electrolytes - 1M $NaCF_3SO_3$:G2 and $NaPF_6$:G2 (prepared by dissolving the respective salts in G2 within a glovebox), allowing for a comprehensive analysis of electrochemical performance factors in terms of the plating and stripping processes that govern the working principle of anode free sodium cells. Regarding the anode-free architecture, our approach is presented in the figure below.

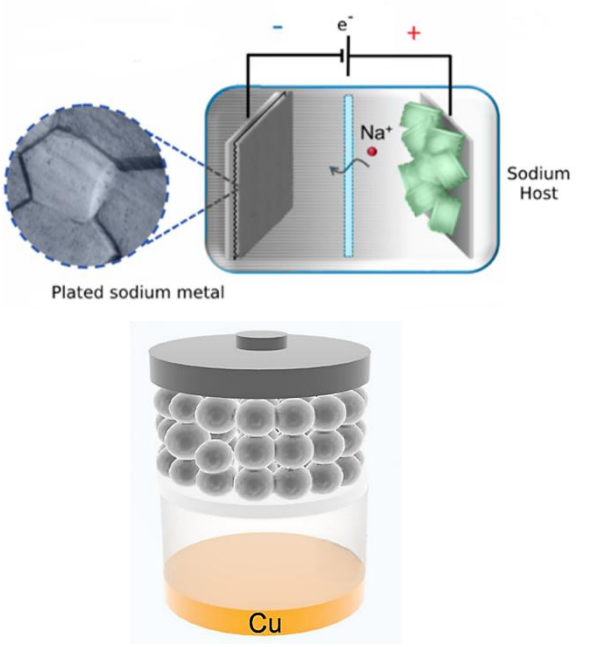

Fig. 1. Simplified schematic of an anode-free Na cell design, adapted from Nano Lett. Adam P. Cohn, 2017, 17, 2, 1296–1301 [Ref. 12].

In this study, all manipulations were performed in a glove box under an argon atmosphere to maintain an inert environment, preventing any degradation of the materials, especially the sodium metal electrodes, which are highly reactive and sensitive to moisture and oxygen.

This controlled assembly environment is essential for ensuring the integrity and reproducibility of the experimental results. Figure 2 shows the basic structure and configuration of the cells used in our experiments.

Fig. 2. 2032-coin cell assembly components: 1-Celgard separator, 2-half of coin cell case, 3-copper electrode inside coin cell case, 4-spring, 5-spacer, 6-Na metal electrode.

The assembly process began with the preparation of CR2032 stainless steel cases, which act as the outer shell and provide structural support for the cells. All cases were made from 316-grade stainless steel, known for its excellent corrosion resistance and mechanical strength—key properties to ensure the long-term stability of the assembled cells under various testing conditions. They were dried in a vacuum chamber at 60 degrees overnight. Consistency in the cell casings was maintained throughout the study to eliminate any variability that could arise from different materials or manufacturing processes.

The choice of separator is a critical element in cell design, influencing performance, safety, and cycle life. In this study, the Celgard 2325 separator, with a diameter of 19 mm, was used to ensure complete physical separation between the copper and sodium electrodes, effectively preventing short circuits, particularly during the sealing of the test cell. Although alternative separators, such as ceramic and glass fiber, were evaluated for their potential to improve stability and ionic conductivity, they did not provide satisfactory results in terms of electrolyte wettability or interfacial stability. As a result, Celgard 2325 was

selected as the optimal separator, offering the best combination of mechanical strength, chemical stability, and electrochemical performance.

The sodium metal electrodes (chips) were presented as individually foil-wrapped discs, each with a diameter of 15.6 mm, a thickness ranging from 0.4 to 0.5 mm, and a purity of 99.7%. Given the high reactivity of sodium metal, particularly with air and moisture—leading to the rapid formation of sodium hydroxide or carbonate—extreme caution was exercised during handling. The protective foil was removed prior to cell assembly to minimize exposure to any residual oxygen or moisture, even within the glove box, ensuring a pristine surface on the sodium electrode. This approach helped mitigate the risk of dendrite formation and ensured the consistency of the initial electrochemical performance.

The preparation of the copper substrates was a crucial step in the assembly process. Copper electrodes were punched from commercially available copper foil with a thickness of 14 μm. After being cut to a diameter of 16 mm, the electrodes underwent a meticulous cleaning protocol. Initially, they were immersed in an ethanol-filled glass container and subjected to ultrasonication for 20 minutes to remove surface contaminants, such as oils, oxides, or particulates, which could hinder the uniform deposition of sodium during cycling. Following a 10-minute air-drying process to eliminate residual ethanol, the electrodes were further dried under vacuum at 70°C overnight to ensure the removal of any remaining moisture. The dried electrodes were then transferred into the glove box to maintain a contamination-free environment.

The electrolytes were prepared directly inside the glove box to preserve the anhydrous and oxygen-free atmosphere. Two electrolyte formulations were used in this study: 1M sodium trifluoromethanesulfonate ($NaCF_3SO_3$) and 1M sodium hexafluorophosphate ($NaPF_6$), dissolved in G2 solvent. The selection of these electrolyte compositions was based on their favorable electrochemical stability and ionic conductivity, both of which are essential for the optimal performance of sodium metal batteries. The electrolytes were prepared by carefully weighing the required amounts of salts and solvents, followed by thorough mixing in sealed vials until complete dissolution was achieved. The resulting solutions were clear, indicating that the salts were fully dissolved, and the electrolytes were ready for use.

For the cell assembly, a volume of 30 μL of electrolyte was used for each cell. After assembly, the cells were inspected to ensure no visible defects, such as misalignment or leakage. All cells were allowed to rest for 24 hours prior to electrochemical testing. This resting period ensured that the electrolyte fully wetted the electrode/separator surfaces, aiding in the formation of a stable solid-electrolyte interphase (SEI). The SEI plays a critical role in stabilizing both the

copper and sodium metal surfaces during cycling, helping to prevent excessive side reactions and dendrite formation—common failure modes in sodium metal batteries. The electrochemical testing was focused on galvanostatic cycling. These tests were performed to assess the performance, stability, and efficiency of the anode-free sodium-ion cells under various operating conditions, offering valuable insights into the feasibility of this innovative cell design for practical energy storage applications.

3. Results and discussion

The electrochemical characterization was carried out on three cells of each type in parallel, and under the same conditions at room temperature. Coulombic efficiency (CE) is an important metric for evaluating the performance of sodium metal cells, particularly in assessing the reversibility of the plating and stripping processes. CE is defined as the ratio of the charge required for oxidation (stripping) to the charge used for reduction (plating) during a complete electrochemical cycle. During the plating process, electrochemical decomposition of the electrolyte can reduce the average CE, and an ideal value would approach 100%. Incomplete stripping, which can result from the formation of "dead sodium" (dendrites that detach from the working electrode during stripping), also contributes to a decrease in CE. Certain negative phenomena, such as short circuits caused by dendritic growth that are quickly interrupted or anodic side reactions, can lead to an inflated CE without providing any real benefit to the system. Additionally, fluctuations in efficiency between cycles may occur if dead sodium reconnects in later cycles. Thus, while CE is an important measure, it does not fully capture all factors influencing the cell performance and may not provide a complete characterization.

Despite the additional complexities, full plating-stripping cycling remains the standard in many studies due to its simplicity and alignment with widely accepted protocols. This approach allows researchers to isolate the effects of different substrates and other variables. Therefore, this study adhered to the standard procedure, performing complete stripping to 1 V after each deposition cycle. Although some issues arose with a few cells—likely due to impurities or damage during handling—the results are promising. This reinforces the importance of careful attention to each step of the process, from material preparation to cell assembly. Variables such as temperature, cycling parameters, and even the resting period before testing can significantly influence the results.

Figure 3 presents the results after 2000 and 1650 cycles, respectively, for two Cu-Na cells, achieving impressive coulombic efficiency (99.99% over 2000 cycles) with the two electrolytes discussed. The data shows consistent cycling behavior when cells are assembled under well-controlled conditions with

thorough handling. Although these conditions may delay failure, the actual lifetime of the cells remains inherently uncertain and is subject to statistical variations. This highlights the crucial role of SEI formation and its long-term impact on the performance of the cell.

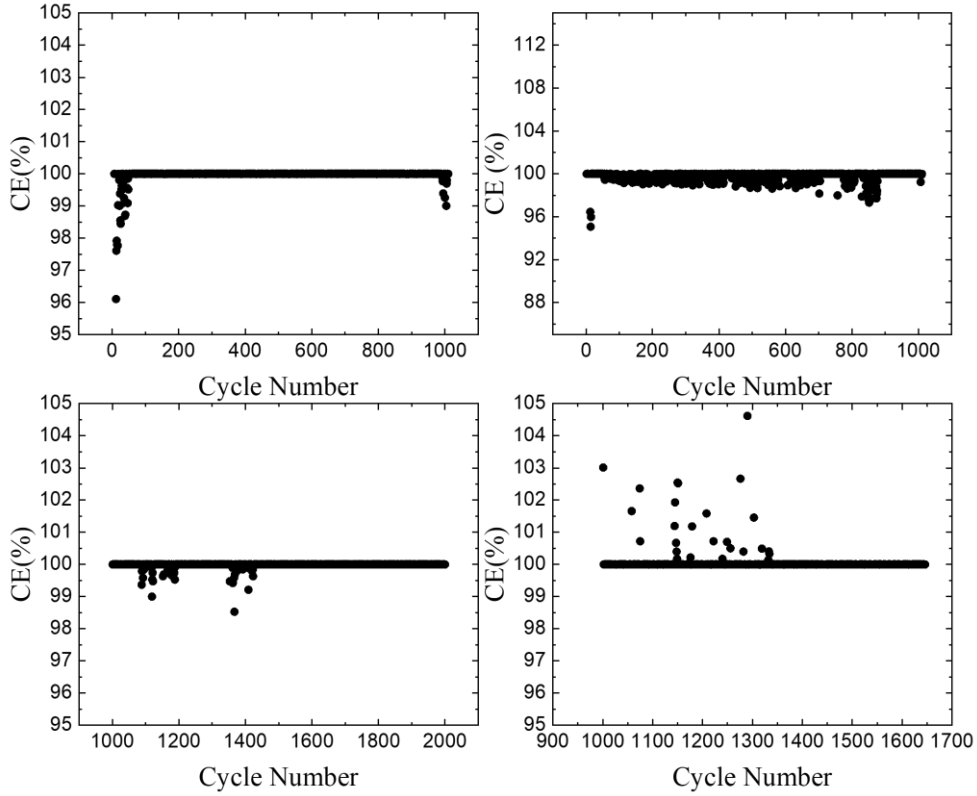

Fig. 3. Coulombic efficiency evolution with cycling for two Cu-Na cells using 1M $NaPF_6$:G2 and 1M $NaCF_3SO_3$:G2 electrolyte showing near perfect coulombic efficiency. The graphs are split in two groups because we did rounds of 1000 cycles per sessions.

The long-term performance of anode-free Na configurations is critically conditioned by interfacial instabilities that emerge after extended cycling. The most prominent mechanism involves the continual restructuring of the solid electrolyte interphase, which forms dynamically during each plating/stripping cycle. Because the SEI is repeatedly fractured by volumetric fluctuations of freshly deposited sodium, soluble decomposition fragments are released into the electrolyte, triggering secondary reduction pathways and leading to progressive thickening and increased impedance. This evolving SEI consumes both electrolyte and sodium inventory, thereby lowering the Coulombic efficiency and accelerating capacity fade.

In parallel, under non-uniform current distributions at the Na deposition front, preferential growth of sodium protrusions occurs. These protrusions, initially mossy in morphology, may evolve toward filamentary dendrites under sustained cycling. Such dendritic structures not only induce local field enhancements that destabilize further deposition but also threaten separator penetration, potentially creating soft or hard short circuits. The interplay between unstable SEI chemistry and morphological inhomogeneity of sodium deposits therefore represents a self-reinforcing degradation loop, in which the SEI fails to passivate effectively and dendritic growth exacerbates interfacial heterogeneity.

This combined scenario highlights why even cells displaying initially stable electrochemical signatures may undergo rapid performance collapse after a critical cycle number, and underscores the necessity of electrolyte engineering, artificial interphase stabilization, or 3D current collector architectures as strategies for mitigation.

As shown in Fig. 4, the cells were cycled between 0V and 1V. The cycling profiles demonstrate remarkable stability from the initial cycles to the data collection point.

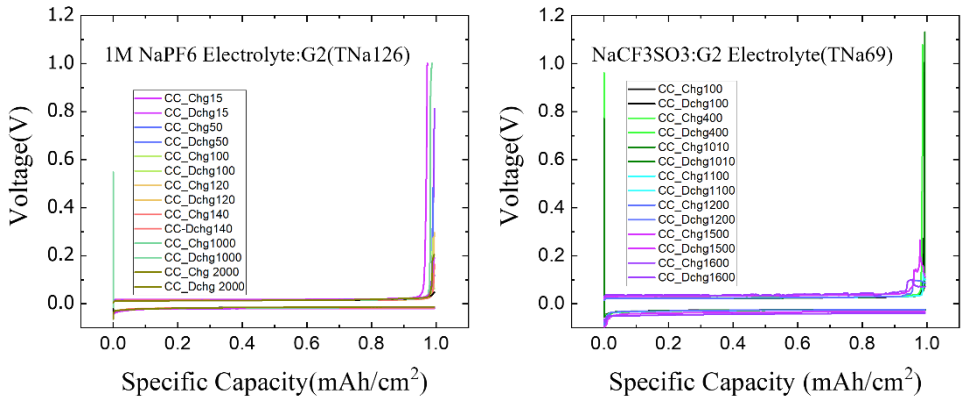

Fig. 4. Cycling profiles for the studied Cu-Na cells with 1M $NaPF_6$:G2 and 1M $NaCF_3SO_3$:G2 electrolytes, cycled at a current density of 1.5mA/cm^2.

Minor deviations or anomalies can be seen in the later cycles, represented by outlier points in the plots. These fluctuations are likely due to incomplete stripping or the formation of dead sodium, which eventually ceases to participate in the electrochemical reactions. However, this issue was transient, as stripping was completed in the next cycle, and normal cycling behavior was quickly reestablished. The voltage hysteresis (the difference between charge and discharge curves) remained minimal, especially during the early cycles. This low hysteresis suggests efficient energy storage and retrieval with minimal energy loss. Despite

some minor deviations, the overall performance remains robust, with most cycles showing stable, reproducible voltage profiles. This indicates that both the electrolyte and cell design are effective at maintaining a stable sodium metal electrode, even in an anode-free configuration.

4. Conclusions

This study provides a comprehensive evaluation of anode-free type sodium metal cells, demonstrating their practical feasibility and significant promise as sustainable energy storage solutions. By employing a simplified cell architecture based on a bare copper electrode paired with an optimized electrolyte system, we successfully attained stable cycling performance over 2000 cycles at a current density of 1.5 mA/cm^2, alongside remarkably high Coulombic efficiencies (~99.99%). Our comparative analysis of two electrolyte formulations, 1M $NaPF_6$ and 1M $NaCF_3SO_3$ in diglyme solvent, highlights electrolyte composition as a determining factor for the effective management of sodium plating/stripping processes. While NaPF6 provides excellent ionic conductivity and facilitates efficient plating kinetics, its high moisture sensitivity poses considerable practical challenges, potentially leading to suboptimal SEI formation and cycle-life reduction. Conversely, $NaCF_3SO_3$ exhibits encouraging properties that warrant further systematic exploration, particularly regarding SEI stability and reversibility of sodium deposition. Future studies should aim to optimize these electrolyte systems further, examining novel additives and tailoring solvent-salt interactions to mitigate dendrite formation and enhance long-term electrochemical stability. Addressing these key aspects will be vital for overcoming current limitations, thereby positioning anode-free sodium metal technology as a viable, high-performance alternative to conventional lithium-ion and sodium-ion battery systems. In the context of sodium-ion systems, the selection of salt plays a decisive role in defining both the interfacial chemistry and the long-term stability of the electrochemical cell. Sodium hexafluorophosphate ($NaPF_6$) has been widely employed due to its high solubility in common carbonate-based solvents and its ability to promote the formation of a relatively stable solid electrolyte interphase (SEI). The decomposition of PF_6^- anions often leads to inorganic species such as NaF, which contribute to mechanically robust and ionically conductive SEI layers.

However, $NaPF_6$ exhibits limited thermal stability and can undergo hydrolysis, releasing corrosive HF species that may accelerate the degradation of both electrode surfaces and electrolyte components. By contrast, sodium trifluoromethanesulfonate ($NaCF_3SO_3$) demonstrates superior thermal stability and a lower tendency toward hydrolytic decomposition, which improves its safety profile and extends its electrochemical window. The anion ($CF_3SO_3^-$) typically yields organic-rich SEI films, which may be less mechanically rigid but provide

favorable ionic conductivity and more uniform coverage on sodium surfaces. Importantly, in terms of compatibility with copper substrates, $NaPF_6$-containing electrolytes may trigger surface corrosion processes through HF formation, compromising the integrity of the current collector. $NaCF_3SO_3$, in contrast, minimizes such corrosion pathways due to the absence of HF-generating decomposition routes, thereby preserving the electrochemical performance of copper-based anodes. When compared directly, $NaPF_6$ offers better established SEI-forming capabilities but at the expense of reduced thermal stability and potential substrate degradation, whereas $NaCF_3SO_3$ provides improved safety and substrate compatibility, albeit with an SEI that may require optimization to achieve sufficient mechanical protection during extended cycling.

While coin cell architectures serve as a convenient platform for the initial evaluation of electrode–electrolyte interactions, significant challenges emerge when such systems are scaled toward larger pouch or cylindrical formats. One primary difficulty lies in the increased heterogeneity of ion transport across thicker electrodes, where uneven current distribution may exacerbate local polarization, leading to inhomogeneous sodium deposition and accelerated interfacial degradation.

Furthermore, electrolyte consumption, which is often negligible in coin cells, becomes critical in larger systems due to the need for controlled wetting and uniform SEI formation across extended electrode surfaces. The stability of the SEI, already sensitive to fluctuations in temperature and cycling conditions, is further stressed under scaled-up operation, where thermal gradients and mechanical stresses are more pronounced. Sodium dendrite formation, manageable in limited laboratory settings, presents amplified safety risks when translated into high-capacity cells, especially given the reduced tolerance for localized short circuits.

Another challenge concerns the compatibility of copper or alternative current collectors, as minor corrosion effects observed in coin cells can evolve into substantial performance losses in larger geometries where collector integrity directly influences electronic conductivity and mechanical cohesion. Finally, the engineering aspects—such as electrolyte volume optimization, gas evolution management, and thermal regulation—introduce layers of complexity absent at the coin cell level, thus underscoring the necessity of integrated design strategies that couple electrochemical insights with robust cell engineering.

Acknowledgement

This work received funding from the Romanian Ministry of Research, Innovation and Digitalization under Romania's National Recovery and Resilience Plan (PNRR) - Pillar III, Component C9, Investment I8

(PNRR/2022/C9/MCID/I8), grant no. 760113/23.05.2023 (ToNaBatt), and from the component project PN 23 15 02 01 (BatNaS) under funding 20N/2023.

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