# Evaluating Cycle Stability in Aluminum-Graphite Battery Systems: Current Insights and Prospective Improvements

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**Abstract**

Aluminum ion batteries are emerging as a promising solution for future energy storage due to their high energy density, cost-efficiency, and environmental friendliness. This study focuses on evaluating the cycle stability and overall performance of Aluminum/graphite batteries using flexible, binder-free graphite paper as the cathode material. Electrochemical performance, including charge-discharge cycling, is assessed through extensive experimental testing. Our findings demonstrate that the use of binder-free graphite paper enhances electrical conductivity and structural stability, leading to improved battery performance and longevity. This research provides valuable insights into the development of high-performance Aluminum/graphite batteries and looks toward future prospects for their broader adoption in sustainable energy applications.

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**Аннотация**

Алюминий-ионные аккумуляторы становятся перспективным решением для будущего хранения энергии благодаря их высокой энергетической плотности, экономичности и экологичности. В данном исследовании основное внимание уделяется оценке стабильности циклов и общей производительности алюминий/графитных аккумуляторов с использованием гибкой, не содержащей связующих графитовой бумаги в качестве катодного материала. Электрохимическая производительность, включая циклирование заряда-разряда, оценивается посредством обширных экспериментальных испытаний. Наши результаты показывают, что использование графитовой бумаги без связующих улучшает электрическую проводимость и структурную стабильность, что приводит к повышению производительности и долговечности аккумуляторов. Данное исследование предоставляет ценные сведения для разработки высокопроизводительных Al/графитных аккумуляторов и рассматривает перспективы их более широкого применения в устойчивых энергетических системах.

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**Аннотация**

Алюминий-ион аккумуляторлари юқори энергия зичлиги, иқтисодий самарадорлиги ва экологик хавфсизлиги туфайли келажакда энергия сақлашнинг истиқболли ечими сифатида намоён бўлмоқда. Ушбу тадқиқотда алюминий/графитли аккумуляторларнинг цикл барқарорлиги ва умумий самарадорлигини ҳамда катод материали сифатида эгилувчан, боғловчисиз графит қоғозидан фойдаланиб баҳолашга эътибор қаратилган. Заряд-разраяд циклини ўз ичига олган электрокимёвий самарадорлик кенг қамровли экспериментал синовлар орқали баҳоланди. Топилмаларимиз шуни кўрсатадики, боғловчисиз графит қоғозидан фойдаланиш электр ўтказувчанлик ва структуравий барқарорликни яхшилайди, бу эса аккумуляторнинг ишлашини ва барқарорлигини оширади. Ушбу тадқиқот юқори самарадоликка эга алюминий/графитли аккумуляторларни ишлаб чиқиш борасида муҳим маълумотларни тақдим этади ва шунингдек уларни барқарор энергия тизимларида янада кенгроқ қўлланилиш истиқболларини ҳам назарда тутади.

***Key words:*** *Aluminum ion batteries, next generation, energy storage systems, lithium ion batteries, graphite cathode*

***Ключевые слова:*** *алюминий-ионные аккумуляторы, следующее поколение, системы хранения энергии, литий-ионные аккумуляторы, графитовый катод.*

***Калит сўзлар:*** *алюминий-ион аккумуляторлари, кейинги авлод, энергия сақлаш тизимлари, литий-ион аккумуляторлари , графитли катод*

## Introduction

Lithium-ion batteries (LIBs) have become a cornerstone technology in modern energy storage, widely utilized in electric vehicles (EVs) and portable electronics [1-3]. This widespread adoption is largely due to their impressive specific energy, which translates to a higher amount of energy stored per unit mass, their long service life, and their efficiency in terms of energy conversion and storage. Additionally, LIBs are valued for their lightweight nature, which is a crucial factor in applications where weight is a significant concern, such as in electric vehicles.

However, despite these advantages, LIBs face several critical challenges that limit their performance and safety under extreme conditions.[4-8]. High temperatures can lead to thermal runaway, a situation where an increase in temperature causes a further increase in temperature, potentially resulting in a fire or explosion. Safety is another major issue, as the potential for overheating and thermal runaway poses significant risks. Furthermore, the cost of LIBs, while decreasing, remains a concern, particularly for large-scale applications. The environmental impact of battery disposal and recycling is also significant, as improper handling can lead to the release of toxic substances. Sustainable sourcing of raw materials is crucial, given that lithium, cobalt, and other elements used in these batteries can be environmentally damaging to extract. Additionally, there is an ongoing need for the development of improved battery management systems to enhance reliability, longevity, and safety.

In this context, Aluminum ion batteries (AIB) are emerging as a promising alternative. These batteries present several potential advantages over their lithium-ion counterparts. For instance, they offer a high theoretical volumetric capacity, which means they can store a considerable amount of energy within a given volume. [9-13]. They also boast faster charging times, making them suitable for applications requiring quick recharging. Aluminum, a key component of AIBs, is more abundant and less expensive than lithium, which can help lower production costs[14]. Another significant advantage of AIBs is their superior safety profile. AIBs are less prone to overheating and thermal runaway, which are major safety concerns associated with LIBs. This enhanced safety, combined with a longer lifespan, positions AIBs as a viable alternative for various applications.

However, the application of aqueous electrolytes in AIBs, while cost-effective, comes with its own set of challenges. Hydrogen evolution and passive film formation are significant issues that hinder the widespread adoption of these batteries. Hydrogen evolution can lead to gas build up, which compromises the battery's efficiency and safety. Passive film formation on the electrode surface can impede ion transport, affecting overall battery performance. These issues highlight the need for the exploration of non-aqueous electrolytes, which could potentially address these limitations and improve both the performance and durability of AIBs.

One of the primary challenges in advancing AIB technology is the identification of suitable cathode materials that offer both high performance and stability. Extensive research has been directed towards various cathode materials, including metal oxides, metal sulfides, and carbon-based materials. Metal oxides and sulfides, while exhibiting high initial capacities, often struggle with stability over extended cycling periods. In contrast, carbon-based materials, particularly graphite, have shown promising results.

Graphite stands out due to its exceptional electrochemical stability, high conductivity, and long cycle life, making it an ideal candidate for enhancing the performance and durability of AIBs. Its high conductivity ensures efficient electron transport, which is crucial for the battery's operation, while its stability and longevity address critical issues related to energy density and battery life, positioning graphite as a key material in advancing AIB technology [15-17].

In this research, we focused on utilizing flexible, binder-free graphite paper as a cathode material in AIBs. Graphite paper offers distinct advantages by simplifying handling and integration into various battery configurations, thus enabling more versatile and adaptable battery designs. By eliminating the need for binders, the overall weight and complexity of the electrode might be reduced, potentially contributing to better battery performance.

The binder-free nature of graphite paper facilitates direct contact between graphite particles, leading to improved electrical conductivity, which supports the rapid movement of electrons and ions during charge and discharge cycles. Additionally, the flexibility of the graphite paper allows it to accommodate volume changes that occur during cycling, enhancing its structural stability and extending the battery's lifespan.

This research aims to contribute to the development of more efficient, reliable, and cost-effective AIBs, paving the way for their broader application and adoption in various energy storage solutions.

## Experimental details

### *Cell assembly*

In our experimental setup, 80-micron thick, commercially available, binder-free flexible graphite paper was selected as the cathode material for the AIB, assembled within a Swagelok cell. The graphite paper was meticulously cut to the required dimensions and subjected to a drying process at 100°C to remove any contaminants and moisture, thereby preserving its integrity and enhancing its performance. Subsequent to drying, the graphite paper was transferred to an argon-filled glovebox to prevent exposure to air and moisture. A separator, treated using the same drying procedure to maintain consistency, was also introduced into the glovebox along with the graphite cathode for assembly.

Inside the glovebox, aluminum foil was cut to match the dimensions of the electrode material to function as the anode, ensuring precise alignment and fit within the cell. The electrolyte comprised a mixture of aluminum chloride ($AlCl_3$) and 1-ethyl-3-methylimidazolium chloride (EmimCl), prepared in a molar ratio of 1.7:1. This ratio was selected based on previous research indicating optimal ionic conductivity and stability for AIBs.

### *Electrochemical Testing*

Following cell assembly, the battery was carefully transported to the electrochemical measurement setup. A galvanostat was utilized for precise control and monitoring of the AIB performance. To assess the cycling stability and specific capacity of the graphite cathode, long-term stability tests were conducted using at a fixed current density.

### *Results and Discussion*

The cycling stability of the AIB utilizing graphite as the cathode material was rigorously evaluated through extended long-term stability testing, providing a comprehensive understanding of the battery's performance metrics over prolonged operational periods. Figure 1 illustrates the specific capacity and Coulombic efficiency over 150 cycles, offering critical insights into the electrochemical behavior and stability of the system.

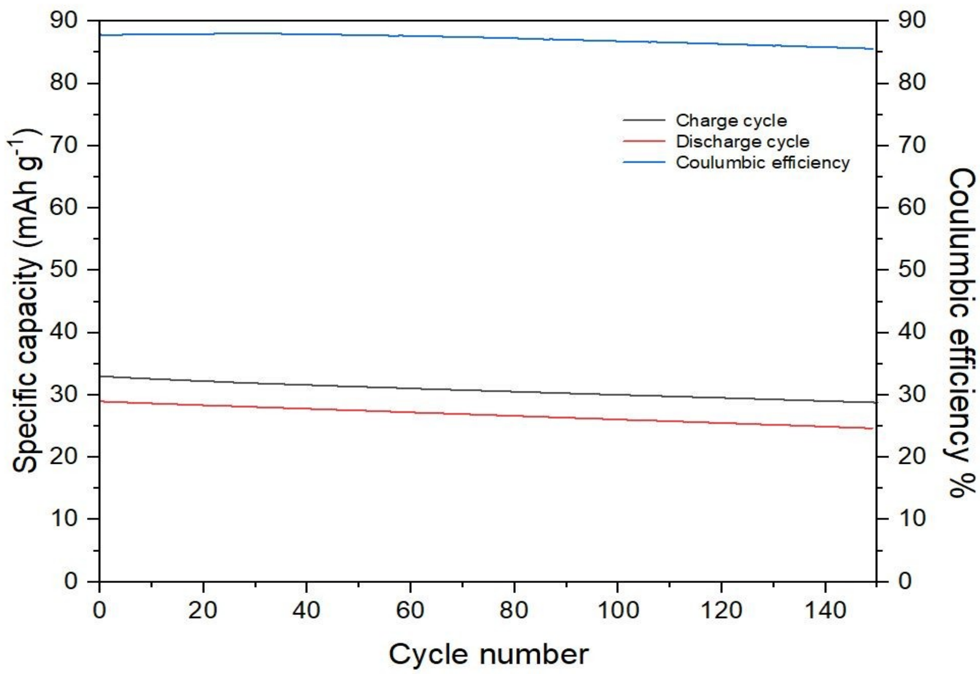


***Fig.1. Electrochemical stability test of graphite cathode***

During charging, tetrachloroaluminate ($AlCl_4^-$) anions intercalate into the graphite structure, and during discharging, they are released back into the electrolyte.

The specific capacity, as determined from the charge and discharge profiles, is a key parameter reflecting the energy storage capability of the battery. Initially, the charge capacity was approximately 33 mAh $g^{-1}$. Over 150 cycles, this capacity gradually decreased, stabilizing around 28 mAh $g^{-1}$. Similarly, the discharge capacity started at approximately 30 mAh $g^{-1}$ and declined to about 25 mAh $g^{-1}$ by the end of the testing period. This gradual reduction in specific capacity can be attributed to several factors. The repeated intercalation and de-intercalation of aluminum ions into the graphite matrix involve the continuous insertion and removal of ions from the electrode material. Over time, this cyclic process can induce significant structural fatigue and eventual degradation of the graphite cathode. This degradation manifests as microstructural changes, such as the development of cracks or pulverization within the graphite layers. These alterations compromise the integrity of the electrode material and lead to a reduction in its effective capacity.

Additionally, prolonged cycling can result in the decomposition of the electrolyte, creating by-products that hinder ion transport within the battery. These by-products can form insulating layers or other obstructions that impair the efficient movement of ions between the electrodes, further diminishing the battery's performance. Furthermore, the formation of a solid electrolyte interphase (SEI) layer on the graphite surface is a critical aspect of stabilizing the electrode-electrolyte interface. While the SEI layer plays an essential role in protecting the electrode material, its growth can sometimes become excessive or unstable. An overly thick or unstable SEI layer can act as a barrier to ion movement, contributing to irreversible capacity loss and reducing the overall efficiency of the battery.

The graph shows that the Coulombic efficiency remains consistently high, approximately 90%, over 150 cycles. This high efficiency indicates that the majority of charge input during charging is effectively recovered during discharging, demonstrating robust electrochemical reversibility and efficient utilization of active materials. The stable Coulombic efficiency implies minimal detrimental side reactions that could otherwise lead to charge loss and reduced efficiency.

While there is a gradual decrease in specific capacity, which is typical due to material and electrolyte degradation, the consistently high Coulombic efficiency reflects effective charge-discharge processes and minimal side reactions. These results suggest that, although further improvements are possible, the current system already exhibits notable stability and efficiency over extended use.

## Conclusions

The investigation into Al/graphite batteries highlights their potential as advanced energy storage solutions due to their high energy density, cost-effectiveness, and environmental benefits. Our study demonstrates that AIBs with graphite cathodes exhibit considerable performance and stability over extended cycles. The effective intercalation and de-intercalation of $AlCl_4^-$ anions into the graphite structure have been successfully managed. The system maintains a high Coulombic efficiency of approximately 90% across 150 cycles, indicating robust charge-discharge processes. Despite a gradual decrease in specific capacity, attributed to structural degradation and electrolyte decomposition, the overall performance remains promising. The use of flexible, binder-free graphite paper has enhanced the battery's electrical conductivity and structural stability compared to traditional materials.

Future research should focus on several key areas to advance AIB technology. Optimizing electrolyte formulations is essential to address issues with the stability and efficiency. Investigating alternative ways for modifications to the graphite cathode, such as doping or advanced surface treatments, may further enhance structural integrity and capacity retention. Comprehensive electrochemical characterization techniques, including real-time monitoring and post-mortem analysis, are crucial for understanding degradation mechanisms, refining battery design, and advancing performance to overcome current limitations.

As technology progresses, AIBs are expected to become increasingly viable for applications in electric vehicles and grid energy storage. Addressing the challenges identified in this study and pursuing innovative research directions will help realize the full potential of AIBs, contributing to the development of more sustainable and efficient energy storage technologies.

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