# Enhancing electrochemical properties for aluminum-based anode materials for LIBs with PVP-derived carbon protective coating

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*Received 6 Aug. 2025; Revised 03 Oct. 2025; Accepted 16 Oct. 2025; Published 18 Nov. 2025.*
**DOI:** https://doi.org/10.54939/1859-1043.j.mst.IMBE.2025.214-220

## ABSTRACT

*This paper presents a study on improving the electrochemical performance of commercial aluminum powder as a LIBs anode material with a protective shell derived from PVP via a simple process. The fabricated Al@C shows a significant change in surface characteristics. The outer coating prevents the active material from rapid deterioration and maintains capacity over many cycles. CV scans at cycle 200 demonstrated a notable enhancement in the intensity of redox peaks, indicating effective preservation of the active material structure. The coating also influences the lithiation process of the underlying aluminum, leading to a gradual activation of the material during operational. The EIS measurements revealed that the protective coating enhances the SEI layer formation over multiple cycles. The study's findings suggest a possible approach to effectively mitigate the issues related to aluminum as an anode material for LIBs.*

**Keywords:** Aluminum-based anode material; Lithium-ion batteries; Carbon coating; Polyvinylpyrrolidone.

## 1. INTRODUCTION

Aluminum (Al), a widely available and safe metal, emerges as a noteworthy candidate for an anode material. At room temperature, aluminum can form β-AlLi alloy phase (solid solution) with Li, providing a theoretical capacity of 993 mAh/g and the capability to suppress the dendrite formation, which is the root cause of safety concern [1]. Aluminum demonstrates remarkable conductivity and is suitable for extensive processing. Furthermore, the lightweight characteristics of aluminum play a significant role in improving gravimetric energy density. The properties of aluminum make it a suitable choice for an affordable electrode material in LIBs. To successfully introduce this electrode active material to the market, it is essential to address specific technical challenges. Like other alloying-type anode materials (Si, Sn, Mg, etc.), aluminum bulk material undergoes a 97% volume expansion when fully lithiated, as crystal lattices are warped and stretched when lithium diffuses further into the electrode material. During the delithiation process, lithium is extracted from the alloy, leaving behind voids in the material's bulk that cannot be retracted back to the original state. As a result, the crystalline structure of the active material evolves to a porous and amorphous matrix, which is susceptible to fractures, thus causing capacity loss and electrode degradation. To prevent capacity decay and prolong the life span of the aluminum-based anode, it is imperative to maintain structural integrity [2].

A potential solution to those issues involves the development of an outer protective shell. Carbonaceous materials exhibit excellent conductivity, enhanced chemical and electrochemical stability, and distinctive physicochemical properties, making them a promising choice for improving electrode performance in terms of electrochemical properties and stability. Diverse sophisticated carbonaceous materials, including graphene, carbon nanosheets, and carbon nanotubes, have been employed in numerous designs with varying forms and have demonstrated effectiveness as a solution [3]. Nevertheless, these approaches are highly complex and therefore difficult to implement at large scales. Certain authors assert that polymer materials are crucial for the forthcoming advancements in LIBs, as they can serve as precursors for the development of

carbon coatings with notable properties for both electrodes of LIBs [4]. Polyvinyl pyrrolidone (PVP) is distinguished among polymers for its versatility, uniformity, and comparatively low carbonization temperature. PVP typically produces a lower quantity of carbon than certain other precursors, particularly at elevated pyrolysis temperatures. However, the carbon membrane derived from PVP exhibits a high surface area, which can help reduce volume changes, making it advantageous for battery applications [5]. Additionally, PVP contains nitrogen in its structure, which remains in the carbon coating after carbonization. The formation of nitrogen-doped carbon results in improved electrochemical, catalytic, and surface properties compared to undoped carbon materials. Therefore, PVP is frequently chosen as a carbon precursor to enhance the performance of electrode active materials in energy storage applications [6].

This paper presents an exploratory study aimed at enhancing the electrochemical performance of commercial aluminum powder utilized as an anode material for lithium-ion batteries. The approach involves the application of a protective shell derived from a PVP precursor through a simple process, followed by carbonization. Following an investigation into the physicochemical properties, the obtained sample (designated as Al@C) will serve as the active material for electrode fabrication and the assessment of its electrochemical characteristics.

## 2. EXPERIMENTAL SECTION

### 2.1. Sample preparation

A mixture of commercial aluminum powder (2 μm particle size, 99.9% purity) and a PVP solution in ethanol is prepared using a magnetic stirrer until the mixture is dried. The weight ratio of Al and PVP is controlled at 2:1. The raw polymer-coated aluminum is subsequently moved to a tube furnace containing nitrogen gas with a heating rate of 3 degree/min and held at 630 $^{o}$C for a duration of 120 minutes to facilitate good formation of the coating on the aluminum substrate. Following the carbonization, the Al@C material sample is acquired.

### 2.2. Physicochemical characterizations

Surface morphologies of materials are analyzed through scanning electron microscopy (SEM, Hitachi S-4800). Energy Dispersive X-ray analysis (EDX) and elemental mapping are conducted on the same equipment. The crystal structures of the samples are analyzed via X-ray diffraction (XRD) utilizing the Bruker D8 Advance system.

### 2.3. Electrochemical characterizations

A mixture of Al@C material, polyvinylidene fluoride, and carbon black Super P in a weight ratio of 7:2:1 was combined with an adequate amount of N-Methyl-2-Pyrrolidone solvent and thoroughly processed in a ball mill until a uniform black slurry was obtained. The black slurry was applied to the carbon-coated surface of the copper foil substrate using a doctor blade and subsequently dried at 80 °C in a vacuum oven for 24 hours to produce the electrode sheet. The electrode sheet was calendered using a roll press to improve its density and then cut into 10 mm discs. Each electrode disc, controlled to contain approximately 1 mg of active material, was assembled within a CR2032 half coin cell with a lithium metal chip that functioned as both the counter electrode and the reference electrode concurrently. The separator between the two electrodes consists of a porous polypropylene sheet, which has been soaked with a 1M solution of $LiPF_6$ in a 1v:1v:1v mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate. The fabricated electrodes were tested using cyclic voltammetry (CV), galvanostatic charging/discharging (GCD), and electrochemical impedance spectroscopy (EIS). CV and GCD testing use a WonATech-WBCS 3000L32 automated battery recycler. EIS measurements are performed with a Metrohm Autolab PGSTAT302N potentiostat from 100 kHz to 100 mHz at open circuit voltage with a 10 mV voltage amplitude.

## 3. RESULTS AND DISCUSSION

### 3.1. Physicochemical characterizations

Figure 1 displays SEM images that depict the surface properties of the original aluminum powder material relative to the synthesized Al@C material. The unmodified aluminum particles have a mostly spherical shape with a smooth surface, as seen in figure 1a. The SEM images acquired after treatment demonstrate a notable alteration in the surface morphology of the particles, as seen in figure 1b. The surface features of the aluminum particles have shifted from a smooth texture to a rough one. In addition, the smaller particles seem to have formed clusters, entirely enveloped by the covering layer.

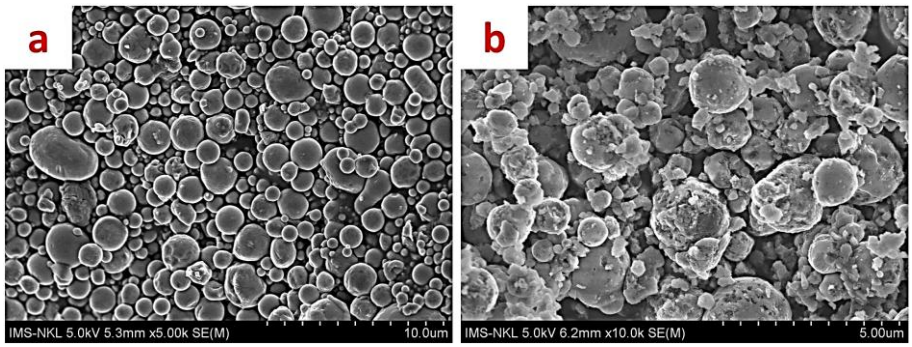


***Figure 1.*** *SEM images of (a) pristine aluminum particles, (b) prepared Al@C material.*

The EDX analysis findings for the Al@C material are shown in figure 2a. The results confirm the presence of the C element in the samples. The elemental mapping images indicate that, in addition to Al and O, which are associated with the natural $Al_2O_3$ thin layer, there is a consistent distribution of C and N along the whole surface of the material sample. The results confirmed that the PVP material is equally distributed across all aluminum particles.

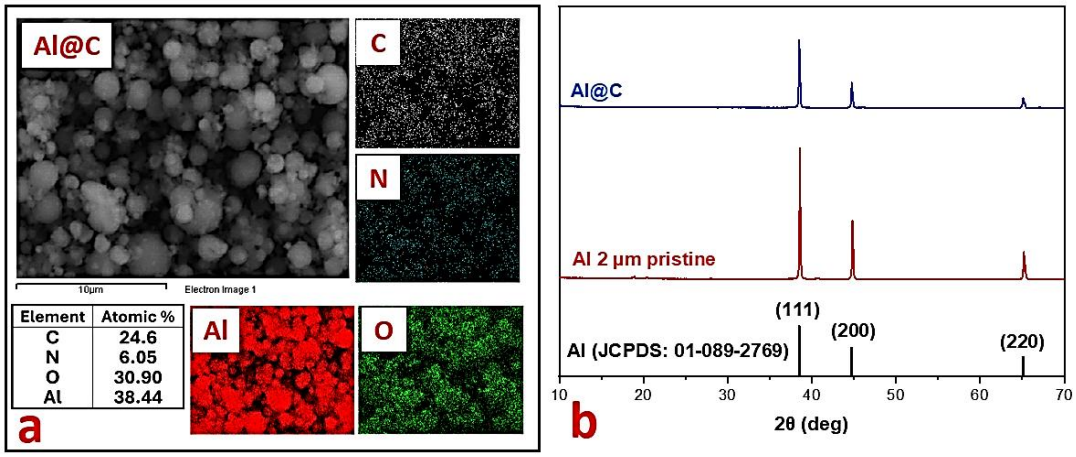


***Figure 2.*** *(a) EDX analysis results of Al@C material, (b) XRD patterns of Al@C and pristine Al.*

Figure 2b displays the XRD patterns for the original aluminum sample and the Al@C material sample, indicating pronounced diffraction peaks at the angular coordinates of 2θ = 38.53, 44.77, and 65.14 degrees, which correspond to the (1 1 1), (2 0 0), and (2 2 0) planes, respectively. This information is consistent with the standard XRD spectrum of aluminum as recorded in JCPDS 01-089-2769. The results demonstrate that the coating on the aluminum particle surfaces does not have a crystalline structure. Nevertheless, the coating creates a uniform layer over the whole aluminum surface, leading to a reduction in the strength of the diffraction peaks for the Al@C material, even though both samples underwent identical XRD measurement parameters.

### 3.2. Electrochemical properties

The preliminary stage of determining electrochemical properties included performing cyclic voltammetry (CV) measurements to investigate the electrochemical behaviors of the electrode. Figure 3 displays the cyclic voltammogram of the Al@C electrode. An evident irreversible peak was seen in the voltage range of 0.5 to 0.75 V (vs. $Li^+/Li$) during the first cycle. This peak signifies the establishing of the SEI layer, which results from the reduction of the electrolyte solution during the first polarization of the electrode. Additionally, a cathodic peak at roughly 0.25 V and its corresponding anodic peak at 0.5 V were observed, indicating the alloying and dealloying processes of aluminum in the composite system ($Li^+ + e^- + Al \rightleftharpoons \beta$-AlLi) [1].

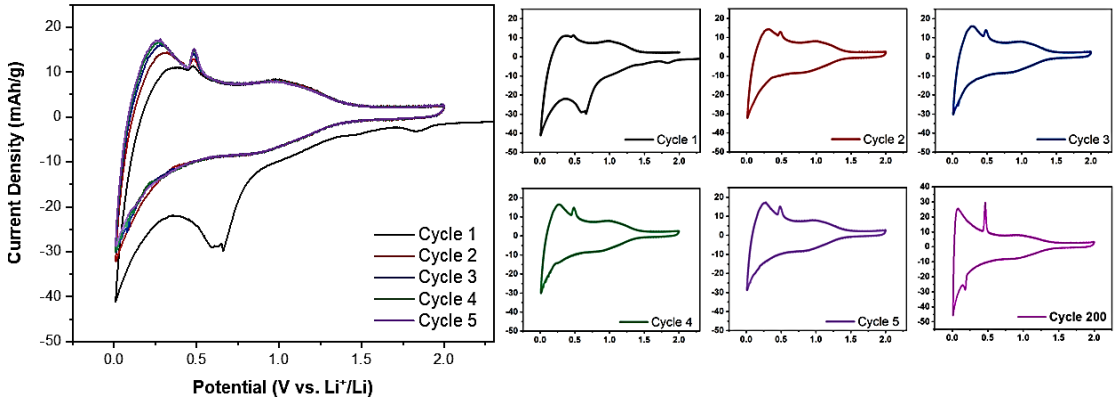


***Figure 3.*** *Cyclic voltammograms of fabricated Al@C electrodes with a scan rate of 0.05 mV/s from 0.01 V to 2 V vs. $Li^+/Li$ (Inset: CV curve after 200 cycles).*

Significant findings were noted about the CV curves of the Al@C material, especially in the intensity increase of the peaks related to the lithiation and delithiation processes of aluminum throughout several cycles. The data reveal that, over the scanning cycles, the alloying and dealloying peaks progressively become more noticeable. A CV scan was performed with the Al@C electrode after 200 charge/discharge cycles, revealing that the alloying/dealloying peaks are markedly more pronounced, indicating significant phase transformation of the aluminum material (refer to figure 3). This is in contrast to previous studies where it has been shown that after a certain number of charging and discharging cycles, the aluminum electrode will transform from a purely faradaic to a "pseudo-capacitive" behavior [2, 7]. This phenomenon emerges as the Al bulk undergoes progressive amorphization, accompanied by a greatly increased specific surface area of aluminum material. The empirical observation suggests that not only does the external layer of Al@C maintain the integrity of the aluminum bulk and successfully preserve capacity during cycling, but it also regulates the lithiation process. In other words, the shell slows down the rate at which lithiation is conveyed to the surface of the Al particle.

Electrodes composed of Al@C were assessed for capacity by galvanostatic charge/discharge (GCD) experiments at a current density of 100 mAh/g. The findings were then compared with those obtained from electrodes composed of pristine aluminum (figure 4a). The results demonstrated that in the first cycle, both materials had comparatively poor coulombic efficiency (CE) due to irreversible development of the SEI layer. In the following cycles, the CE of both electrode samples showed a rapid improvement and consistently remained over 98% throughout the testing period. Nonetheless, the specific discharge capacity of the electrode composed of pure aluminum exhibited a decrease from the first cycle, thereafter, stabilizing at roughly 50 mAh/g after multiple cycles. In contrast, the Al@C electrode had a rather low initial specific discharge capacity (under 60 mAh/g), which was later improved by a steady increase. At the end of the 200-cycle GCD test, it achieved roughly 80 mAh/g, indicating a 30% enhancement compared to the

pristine aluminum electrode (figure 4a). The noted steady increase in capacity is attributable to the function of the coating encasing the electrode material particles. The coating serves as a protective barrier for the electrode and is essential for regulating the diffusion of $Li^+$ ions in both directions. The alloying process transpires gradually and evenly throughout the surface of the material particles as a consequence of that. It is undeniable that uneven lithification causes unequal expansion of the electrode material, hence increasing internal stress and resulting in the premature formation of more severe fractures. When the material bulk is equally alloyed from the surface, along with a spherical particle morphology, the stress distribution will be homogeneous, hence reducing the likelihood of fractures and damage to the electrode material. Furthermore, owing to the more regulated and uniform lithification on the electrode surface, the aluminum particles will be progressively "activated" from the exterior to the interior, leading to a phenomenon of gradually increasing capacity throughout the operational cycles. This explanation clarifies the behavior seen in figure 3 as explained.

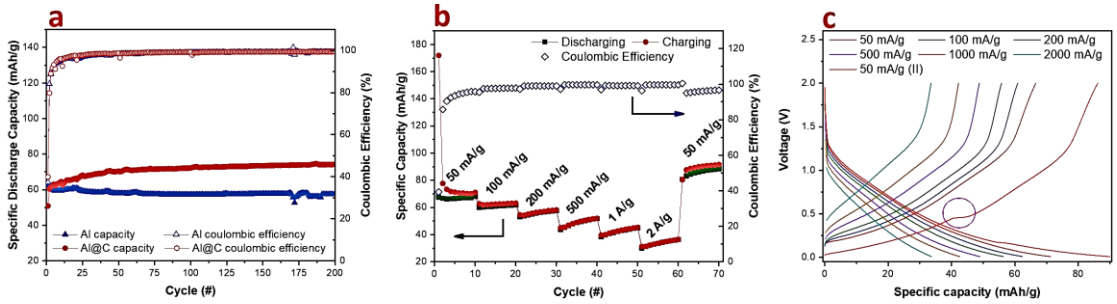


***Figure 4.*** *(a) Galvanostatic charging/discharging performance of Al@C and pristine aluminum electrodes for 200 cycles at 100 mA/g, (b) rate performance of Al@C, and (c) voltage profile of the 5th cycle at each current rate.*

The performance of electrode active materials under different operational conditions was evaluated by measuring the specific capacity of anode electrodes composed of Al@C at current densities of 50, 100, 200, 500, 1000, and 2000 mA/g (figure 4b). The data reveal that the Al@C electrode has notable reversibility, shown by a CE over 95% at most current densities, except during the early cycles when the SEI development occurred. Upon reverting the current density to 50 mA/g, the specific capacity of the Al@C electrode shows a significant improvement compared to its first measurement. This occurrence aligns with the results obtained from capacity measurements during the GCD test and may be attributed to the regulatory and protective roles provided by the coating layer, as previously mentioned. Upon evaluating the voltage profile of the fifth cycle at each current density level in figure 4c, the voltage profile curves precisely depict the capacity characteristics of the electrode. At closer inspection, it is apparent that the voltage profile of the 50 mA/g cycle in the final stage has a wider slope than that of the cycle with the same current density in the first stage (depicted in red and orange in figure 4c, respectively). Furthermore, evidence suggests a voltage plateau at around 0.5 V (vs. $Li^+/Li$), corresponding to the dealloying process of β-AlLi (β-AlLi → $Li^+ + e^- + Al$). This indicates that as the cycle advances, a greater quantity of active material participates in the redox reaction.

The EIS test was performed on the anode electrode made of Al@C material at cycles 1, 5, 10, 100, and 200, as seen in figure 5. During all EIS measurement intervals, the Nyquist plots consistently show a depressed semicircle in the high-frequency range, concluded by an extended straight line in the low-frequency zone. This line signifies the Warburg element, which demonstrates the diffusion properties of active ions in the electrochemical system. Normally, an equivalent circuit is needed to quantify the resistance of each component in the electrochemical system. However, in this case, a comparative assessment of semicircles in the Nyquist plots can provide qualitative insights about the evolution of the cell across cycles. In comparison to cycle 1,

the impedance of the cell in cycle 5 seems to have increased due to the formation of the SEI layer. From cycle 10 onward, the impedance of the cell exhibits a continuous reduction. This spectacle suggests that the alloying/dealloying process occurs more easily as the electrode undergoes repeated charging/discharging. This phenomenon corresponds with the previously mentioned discovery of a progressive capacity gain during GCD after several cycles. This investigation proposes the following explanation: Following many charging and discharging cycles, the aluminum active material experiences volume expansion and undergoes amorphization. The presence of a protective shell aids in containing this amorphous phase and preventing fractures that might result in a reduction in capacity. This amorphous and porous aluminum phase has an increased specific surface area, enhancing the intensity of the redox reaction, resulting in reduced overall impedance, as shown in the Nyquist plots (figure 5), and an augmentation in specific capacity, as seen in figure 4.

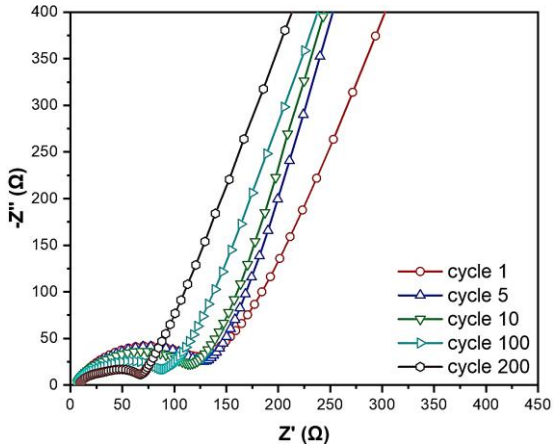


***Figure 5.*** *Nyquist plots of the Al@C electrode at cycles 1, 5, 10, 100 and 200.*

The protective coating layer also contributes to the stabilization of SEI formation. The confinement of all active materials within the protective shell ensures that the SEI layer formed on the outermost surface of Al@C particles remains intact and stabilized throughout the operation. Analysis of the Nyquist plots for electrodes in LIBs frequently presents a secondary semicircle in the high-frequency region, which is generally linked to the interfacial interactions of the SEI layer. However, if the representative resistance of the SEI layer is too low, the visibility of this semicircle may be compromised, possibly overlapping with the semicircle related to the charge transfer process [8]. The EIS measurement results of the Al@C electrode in this study did not display the semicircle typically associated with the SEI layer, suggesting that the coating derived from the PVP precursor improves the properties of SEI layer formation.

## 4. CONCLUSIONS

The commercial aluminum powder was subjected to a simple procedure that included the application of a protective layer derived from PVP precursor, followed by carbonization to produce a carbon-based coating. The electrochemical characterization results of the synthesized material in a half-cell system demonstrate an improvement in capacity compared to the electrode made from unmodified pristine aluminum. Furthermore, detailed electrochemical investigations revealed a significant influence that the coating had on the electrode material. The electrode demonstrated a progressive enhancement in specific discharge capacity during the GCD test. CV scan performed at cycle 200 indicated a notable increase in the intensity of the redox peaks, implying effective preservation of the material structure. The application of the coating serves to protect while also significantly influencing the lithiation process of the underlying aluminum material, leading to a gradual activation of the material during its operational phase. The EIS measurements

demonstrated that the protective coating on the exterior played a significant role in optimizing the formation of the SEI layer over multiple cycles. The study's findings suggest that the application of a protective coating to the electrode material, developed through a simple method, may effectively mitigate the issues related to aluminum materials when used as an active anode material for LIBs. This method may also improve the potential for incorporating this promising electrode material into commercial applications. Based on these findings, it is essential to conduct further investigations in the future to refine the technological parameters.

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## TÓM TẮT

### Cải thiện tính chất điện hóa của vật liệu anode trên cơ sở Al dùng cho ắc quy Li-ion với lớp phủ bảo vệ carbon có nguồn gốc từ PVP

*Bài báo này trình bày một nghiên cứu về việc cải thiện tính chất điện hóa của bột Al thương mại làm vật liệu anode cho LIB với lớp vỏ bảo vệ có nguồn gốc từ tiền chất PVP bằng một quy trình đơn giản. So sánh vật liệu Al@C đã tổng hợp với Al nguyên bản cho thấy sự khác biệt đáng kể về đặc tính bề mặt. Lớp phủ giúp bảo vệ cấu trúc vật liệu của các hạt Al bên trong, ngăn vật liệu hoạt động bị hư hỏng nhanh chóng và duy trì dung lượng qua nhiều chu kỳ. Quét CV ở chu kỳ 200 cho thấy cường độ các đỉnh oxy hóa khử của vật liệu Al tăng lên đáng kể so với các chu kỳ ban đầu, cho thấy cấu trúc vật liệu hoạt động được bảo toàn hiệu quả. Việc phủ lớp vỏ cũng ảnh hưởng đến quá trình liti hóa của Al bên dưới, dẫn đến sự hoạt hóa dần dần của vật liệu trong các giai đoạn làm việc. Hơn nữa, phép đo EIS cho thấy lớp phủ bảo vệ bên ngoài đã cải thiện quá trình hình thành lớp SEI. Kết quả nghiên cứu cho thấy việc sử dụng lớp phủ bảo vệ trên điện cực có thể giảm thiểu hiệu quả các vấn đề liên quan đến Al làm vật liệu anode cho LIB.*

**Từ khoá:** Vật liệu anode trên cơ sở Al; Ắc quy Li-ion; Phủ carbon; Polyvinylpyrrolidone.