

High Performance Rechargeable Aluminium Ion Batteries Enabled by Full Utilization and Understanding of Polyaniline Cathodes

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Abstract

As a renowned conductive polymer, polyaniline (PANI) shows remarkable potential in organic cathode materials for rechargeable aluminium ion batteries (RAIBs). However, existing research has not given sufficient

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understanding and explanation of the structure and states of PANI but failed to achieve ideal electrochemical performance. In this study, we differentiate and investigate for the first time its primary-doped (PANI-1), re-doped (PANI-Re), secondary-doped (PANI-2), and emeraldine based (PANI-EB) forms, meanwhile attempt to enhance the conductivity of PANI-EB using multi-walled carbon nanotubes (PANI-EB@C). Among them, the high-doped PANI-2 and non-doped PANI-EB exhibit theoretical capacity utilization far superior to lower doped PANI-1 and PANI-Re, with both specific capacities reaching approximately 225 mAh g⁻¹ (full capacity utilization rate of 76.53%) at a current density of 1 A g⁻¹, while maintaining capacity retention rates of 92.89% after 2000 cycles and 92.44% after 5000 cycles, respectively. Furthermore, the high-conductivity PANI-EB@C displays a discharge specific capacity of 284 mAh g⁻¹ (full capacity utilization rate of 96.59%), with a capacity retention rate of 91.19% after 5000 cycles. Electrochemical analysis, Gaussian theoretical calculations, ex-situ characterization collectively indicate that the electrochemical performance of doped PANI is positively correlated with the degree of doping-induced conductivity changes, while the unique internal redox process of PANI-EB enhances the release of performance and could be further optimized by the assistant of conductivity medium. This work advances the classification of the electrochemical performance and structural understanding of PANI cathode materials to an extremely high stage, towards the practical application of a low-cost, high-performance, sustainable, and green cathode material in large-scale energy storage devices.

Keywords: Rechargeable aluminium ion batteries; Organic cathode; Polyaniline; Doping; Emeraldine base

1. Introduction

Renewable energy sources are considered evident to be used as the replace of fossil fuels, acting as a reliable solution to meet the energy demand of world in an environmentally friendly and cost-effective manner [1, 2]. However, the intermittent nature of renewable energy sources and the high control requirements of the grid system pose significant challenges for the development and use of large-scale energy storage devices [3, 4]. Although mature lithium-ion batteries have been widely concerned in large-scale energy storage, their application is controversial due to limited reserves and geographical distribution of relevant resources, high cost, limited lifespan, and safety concerns [5, 6]. In a variety of alternative rechargeable alkali metal-ion batteries (sodium, magnesium, aluminium, potassium, calcium and zinc), rechargeable aluminium-ion batteries (RAIBs) have emerged as one of the most promising storage technologies due to their high theoretical capacity (2981 mAh g⁻¹ and 8056 mAh cm⁻³), abundance of aluminium (the third most abundant element in the crust of Earth), low cost, and high safety [7-10].

The main challenge in achieving high-performance RAIBs lies in the selection and preparation of cathode materials [11]. Carbon-based materials as cathode exhibit good cycling performance but suffer from low energy density due to limited discharge capacity and lower power density. Moreover, the preparation of these kinds of inorganic materials is difficult and costly, posing difficulties for subsequent research [12]. Transition metal sulfide/oxide-based cathode show impressive initial discharge specific capacity, but their poor cycling stability results from irreversible phase transitions, unsatisfied rate capability, and high diffusion barrier of interlayer Al³⁺ lead to slow reaction kinetics and hinder their practical applications [13-16]. While the emerging organic materials that break through the limitations of the two types of cathodes above, representing a higher voltage platform and a structure capable of stable reversible reactions, are expected to exhibit higher specific discharge capacity and longer cycle life. To overcome the limitations of the above two classes of cathode materials, organic materials with a higher voltage platform and a structure capable of stable reversible reactions are expected to exhibit higher discharge specific capacity and longer cycle life [17-19].

In organic materials, however, its own Achilles' Heel continues to plague the nascent challengers to conventional materials. Small molecule or monomer cathode materials often inevitably dissolve in ionic liquid electrolytes, and their unstable structure often leads to a rapid decrease in discharge specific capacity after a certain working time, forcing researchers to focus on and try to optimize its molecular structure or to synthesize more complex organizational ones to obtain satisfactory cycling performance [20, 21]. In addition, the poor conductivity also makes it hit a wall everywhere in the test of rate performance, and the limitation on the selection of suitable conductive carrier materials has become one of the most difficult obstacles to break through [22]. In contrast, conductive polymer cathodes, for instance, chain or even network-structured polyaniline (PANI), not only solve the problem of cycling stability through structural strength, but also demonstrate ideal specific capacity by significantly improving conductivity [23, 24]. However, the existing studies of PANI as a cathode for RAIBs are not only vague and confusing in terms of material classification and reaction mechanism, but also neglect to fully develop its full performance potential.

As this dilemma is best described and explained by one famous quote of Alan G. MacDiarmid that "There are as many different types of PANI as there are people who synthesize it [25]." The high degree of uncertainty in the process of organic synthesis and preparation will lead to incomplete understanding or even wrong judgment of the synthesized PANI materials. The lack of adequate characterization also makes it difficult to attain their full demonstration of characteristics and exertion of performance respectively. As a typical conductive polymer, PANI is widely recognized as a wise choice for electrode in the application of energy storage, but it is neglected that its conductivity is achieved through different doping states. The exact status of doping or not and doping complexity is still unclear in most reported samples, and they should actually be identified as preliminary-doped PANI (PANI-1) which is at a relatively ordinary doping level [24, 26]. To be specific on the level of in-depth understanding and identification of PANI itself, research on re-doped PANI (PANI-Re), secondary-doped PANI (PANI-2), and emeraldine-based PANI (PANI-EB) lacks identification of distinction and description of diversity. From the perspective of battery device performance, the lack of

knowledge about the different conductive mechanisms of PANI (especially at different doping levels or in fully redox states), as well as the ambiguity and difficulty of its reaction mechanism in room temperature ionic liquids, hindering PANI from fully realizing its theoretical specific capacity of 294 mAh g⁻¹ [27]. Furthermore, the introduction of other components in some reports, such as other functional groups [28], various metal-based doping ion [29] or composite materials [26], adds complexity and confusion to the structure and mechanism, shifting the focus from exploration of PANI itself.

Based on the above analysis, we believe it is necessary to systematically and thoroughly explore and reveal the doping states, physicochemical properties, electrochemical performance, and redox mechanisms of PANI in order to attempt and derive a deeper understanding of the relationship between doping-conductivity and structure-performance. Therefore, we successfully synthesized five types of PANI materials, including PANI-1, PANI-Re, PANI-2, PANI-EB, and introduced *in-situ* composite growth of multi-walled carbon nanotubes (CNT-MW) to the latter, labeled as PANI-EB@C, among which PANI-Re, PANI-2, and PANI-EB have been rarely mentioned in this field before. Various characterization methods were used to clearly differentiate their unique doping states and structures. For doped PANI, the influence of doping level on conductivity was investigated, and their electrochemical performance in RAIBs was tested. Surprisingly, the complexly doped PANI-2 and the non-doped PANI-EB already exhibited excellent performance, and inspired by the conductivity advantages in doping state, conductivity-improved PANI-EB@C enhanced and closely approached theoretical specific capacity (283 mAh g⁻¹, full capacity utilization rate of 96.59%). On this basis, we attempted to elucidate the different reaction mechanisms of PANI-EB and doped PANI using simulation calculations and high-density *ex-situ* detection. The unique conductivity mechanism in the long chain structure of PANI caused by the complexity of the doping due to the changes in the N-atom functional groups and dopants, and the key role it plays in its own inner redox reaction, determines the outstanding electrochemical properties correspondently. This work fills the current gap in understanding different doping states of PANI in this field and validates the enormous potential of PANI as a cathode material for RAIBs.

2. Results and Discussion

2.1. Theoretical calculations of PANI

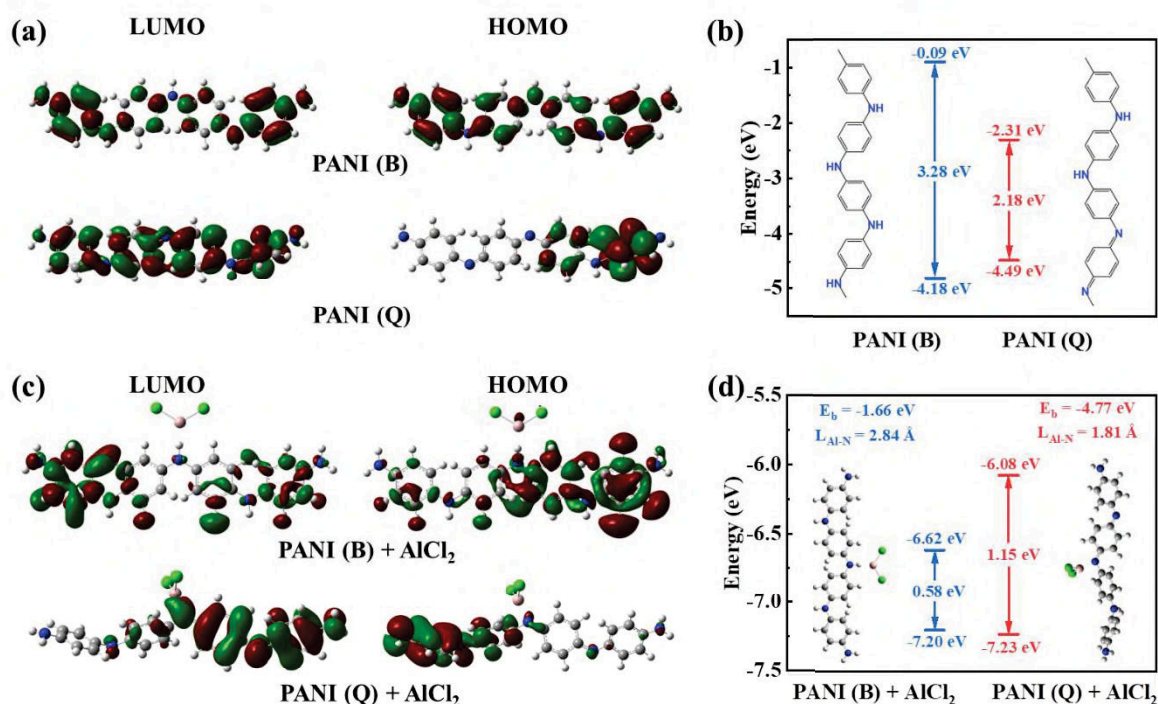


Fig. 1. (a) Frontier orbitals and (b) energy levels with band gaps of doped PANI(B) and PANI(Q), (c) frontier orbitals and (d) energy levels with band gaps of AlCl₃ with PANI(B) and PANI(Q).

In case of preliminary exploration the structures of the two different states of PANI, particularly the different roles played by benzene (B) ring and quinone (Q) ring, theoretical calculations based on the density functional theory with the B3LYP/6-31G (d) basis set were performed [30], and the HOMO/LUMO of frontier orbitals and energy levels with band gaps of PANI (B) and PANI (Q), which in one chain unit with four benzene rings and three benzene rings with one quinone rings, were obtained, as depicted in Fig. 1a and b. The traditional

concept of PANI (B) is commonly formed by the interaction between benzene rings and -NH- with doped groups in a para-position. While based on a 1/2 doping limitation, the chain model of PANI (Q) replaces one out of every four benzene and two for every four -NH- units with one quinone rings and a pair of =N- groups, embodies the characteristics of PANI-EB to a good extent. It is worth noting that the band gap of PANI (B) is wider to approximately 3.28 eV, whereas the one of PANI (Q) is significantly reduced to 2.18 eV. This reduction may be attributed to the transformation from benzene rings to quinone rings, which disrupts the relatively uniform and symmetrical conjugated structure of the molecular chain, leading to a significant destabilization of energy and a decrease in the LUMO-HOMO gap. A smaller band gap implies that the LUMO of the molecule is closer to the HOMO of another molecule in energy, facilitating rapid electron and charge carrier transfer between them. This also suggests a higher likelihood of PANI (Q) accepting electrons, potentially allowing for easier movement of electrons and holes through the material.

The optimized structures of the binding of PANI (B) and PANI (Q) with AlCl_2 groups are shown in Fig. 1c and d. It can be observed that the binding energy (E_b) of PANI (Q) with AlCl_2 groups is -4.77 eV, lower than the -1.66 eV of PANI (B), and the atomic length between Al and N ($L_{\text{Al-N}}$) is 1.81 Å, smaller than the 2.84 Å of PANI (B). These findings indicate that the binding process of AlCl_2 groups with PANI (Q) is more likely to take place compared to PANI (B). Furthermore, the band gap after the binding of PANI (Q) with AlCl_2 groups is 1.15 eV, much higher than the 0.58 eV of PANI (B), suggesting that the detachment process of AlCl_2 groups from PANI (Q) is more likely to occur compared to PANI (B). The propensity of PANI (Q) to undergo spontaneous combination and separation processes with AlCl_2 groups implies its potential as a cathode material for RAIBs. Although we initially believe that emeraldine based PANI (Q) may exhibit better specific capacity and cycle life compared to commonly used doped PANI (B), theoretical simulation results are often so idealistic that not convincing enough. Therefore, further characterization and electrochemical testing are performed to validate the reliability of the computational results.

2.2. Characterizations of PANI

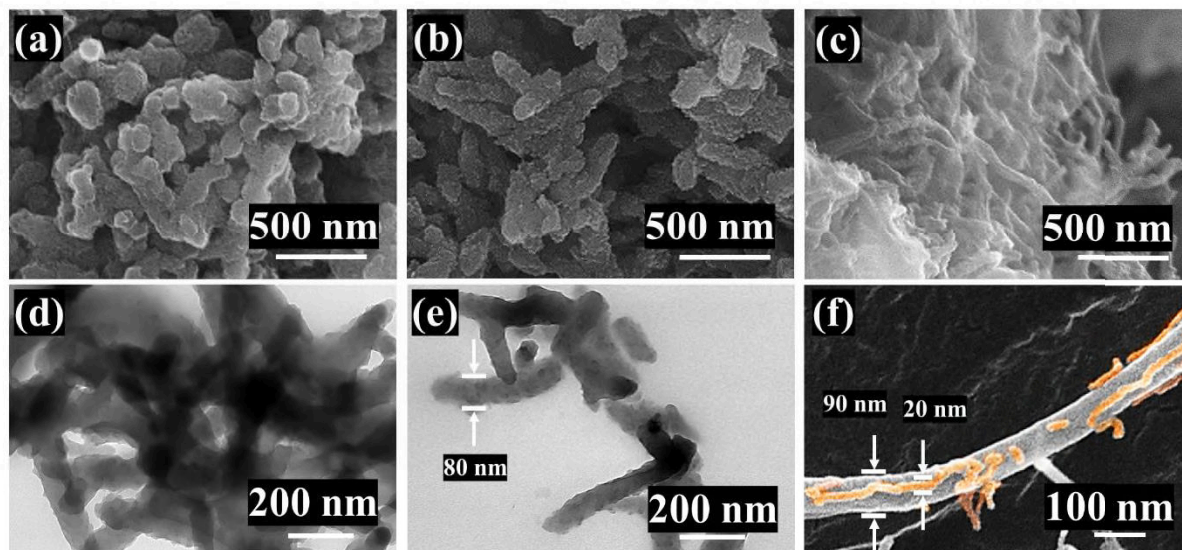


Fig. 2. SEM images of (a) PANI-2, (b) PANI-EB, (c) PANI-EB@C; TEM images of (d) PANI-2, (e) PANI-EB and (f) PANI-EB@C.

SEM and TEM images in Fig. 2 indicate that prepared PANI consists of predominantly grown nanorod-shaped main frameworks with irregularly shaped new particles attached to the surface. In comparison to doped PANI, PANI-EB exhibits a relatively reduced nanorod diameter and a more spacious inter-framework space, which may be the combined result of acid doping and base de-doping processes. Furthermore, the spatial structure of PANI-EB after composite growth with CNT-MW is further improved, with the dispersed chain-like PANI appearing more uniformly, exhibiting a significant improvement in aggregation compared to the distinctly stacked PANI-2 and PANI-EB. The process of polymerization is altered by the induction of CNT-MW materials, as the initiation and growth space of PANI chains are occupied and hindered by their well-dispersed structure. While this may reduce the yield of PANI to some extent, it greatly improves the overall spatial structure of whole composite materials. Careful observation of the details of a single chain reveals that

the PANI chains (orange) grow relatively uniformly on the surface of CNT-MW and the diameter of which also decreased from ~80 nm to ~20 nm, effectively preventing aggregation and exposing as high-proportioned surface area and reaction sites as possible, thereby laying a structural foundation for maximizing the electrochemical performance of the PANI material.

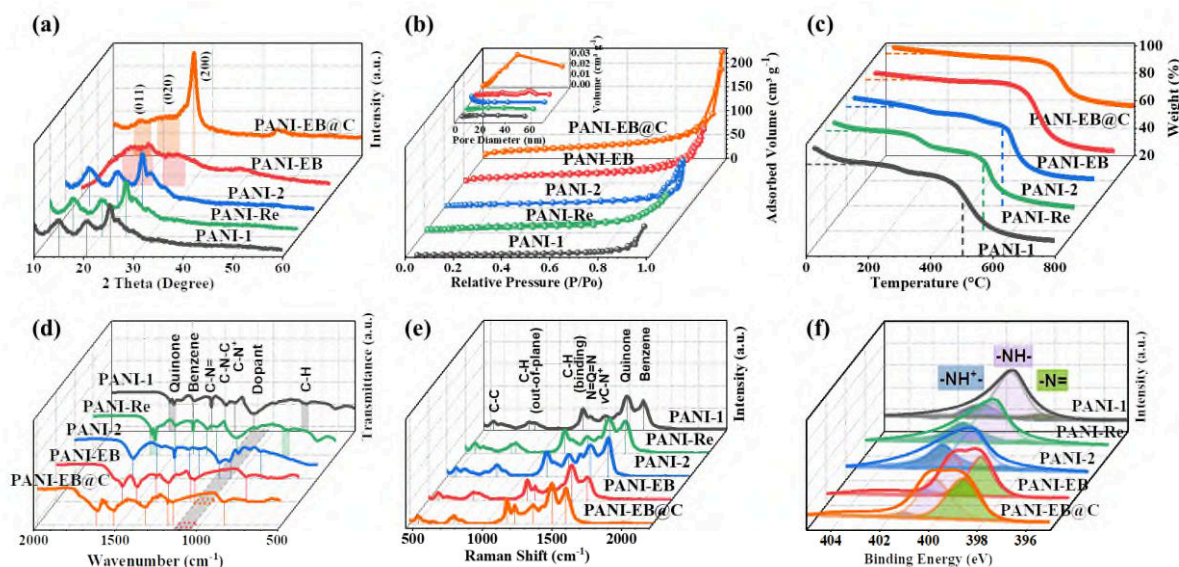


Fig. 3. Structure characterization results of PANI in different states including PANI-1, PANI-Re, PANI-2, PANI-EB, and PANI-EB@C: (a) XRD patterns; (b) N₂ sorption isotherms (the inset showed the pore size distribution); (c) TG curves (N₂ atmosphere, 10 °C min⁻¹); (d) FTIR spectra; (e) Raman spectra and (f) XPS spectra in the N 1s region.

The XRD results of the different PANI materials are demonstrated in Fig. 3a, where PANI-1, PANI-Re and PANI-2 exhibit distinct crystalline structures with well-defined characteristic peaks, indicating the successful synthesis of doped PANI [24, 26]. On the contrast, PANI-EB presents a different pattern, with the absence of clear characteristic peaks and instead a broad feature in the range of 15–20° and 25–30°. This suggests that the emeraldine based state of PANI-EB has undergone de-doping treatment, resulting in a

significant decrease in peak intensity and the formation of a more amorphous structure. The distinct characteristic peak of PANI-EB@C around 26° , as shown in Fig. S1, is introduced by recombination with CNT-MW. The amorphous structure observed in polyaniline-EB suggests some unique properties such as potentially enhanced charge storage, leading to self-healing ability and improved stability[28, 31]. This structural characteristic minimizes the volume expansion and contraction during the charge-discharge process, which is caused by the insertion and extraction of AlCl_2^+ , enhances the stability of the material structure and the cycle life of the cathode.

It can be seen by SEM images that the spatial structure of PANI-EB has not been significantly improved compared with doped PANIs, but the introduction of CNT-MW has greatly changed this phenomenon, which is confirmed by the N_2 sorption isotherms results in Fig. 3b. In the case of doped PANI, it is observed that the absorption volume increases gradually with the increase in doping degree. However, in highly doped PANI-2, a hysteresis phenomenon is observed, which is corresponding to the capillary condensation of the porous adsorbent. It is worth noting that PANI-EB exhibits a similar absorption volume to PANI-2, but the absorption volume of PANI-EB@C is nearly three times higher. This indicates a significant optimization of the spatial structure of PANI-EB, which is further supported by the results of porosity distribution analysis. Comparing PANI-1 and PANI-Re with highly doped PANI-2, it is found that the latter exhibits a higher distribution of micropores in its spatial structure, leading to an improvement in its specific surface area. In contrast, PANI-EB demonstrates a greater presence of mesoporous structures. Moreover, when combined with CNT-MW, the pore distribution of the composite material is significantly enhanced at each pore size. This modification effectively alleviates the issue of PANI materials agglomerating, resulting in a substantial increase in specific surface area and an optimized spatial structure, providing more chemical reaction sites at the spatial level, which could make the great of the electrochemical properties of PANI.

Fig. 3c shows the TG curves of the five PANI samples under a nitrogen atmosphere. The weight loss of PANI-1, PANI-Re, PANI-2, PANI-EB, and PANI-EB@C at 200°C can be defined as their water absorption,

which is 12.1 wt.%, 7.3 wt.%, 7.5 wt.%, 5.6 wt.%, and 5.5 wt.%, respectively. In addition to the dehydration plateau, an extra plateau associated with the removal of the doped acid is observed in the curves of PANI-1, PANI-Re, and PANI-2 (particularly, two additional plateaus are present in the curves due to secondary doping with HCl and chloroform), which is not evident in the PANI-EB and PANI-EB@C until the decomposition stage above approximately 500 °C. This indicates different doping levels of the three doped PANI samples and suggests that the doping level of the latter two intrinsic PANI samples could be considered at an extremely low level (close to zero). Furthermore, due to the presence of stable CNT-MW, the weight loss of PANI-EB@C at 800°C is significantly lower than that of the other PANI samples, at only 43.4 wt.%. As can be further seen from the DTG curve in Fig. S5, in addition to the decomposition of water below 200 °C and the related decomposition of doped-acid groups at about 300 °C, in the decomposition range of 500-600 °C, PANI-EB@C presents relatively superior thermal stability.

In order to further confirm the successful synthesis of PANI in different states, it can be seen from the FTIR spectra data in Fig. 3d (the specific values of each characteristic peak are listed in **Table S1**) that for doped PANIs, the stretching vibration of quinoid ring represented from 1609 to 1635 cm^{-1} gradually increases with the deepening of doping degree, while the stretching vibration of benzenoid ring from 1457 to 1491 cm^{-1} is gradually weakening. In particular, plane bending vibration of C–H formed by protonation from 1046 to 1132 cm^{-1} are observed obviously, and the observation of two types of characteristic peaks in this interval of PANI-2, corresponding to the possible existence of two different doping anions, Cl^- and CCl_3^- , indicating that it is a complex secondary doping, rather than a simple primary process with further increase doping degree. In contrast, for PANI-EB, the characteristic peak intensity in 1590 and 1496 cm^{-1} is basically the same, indicating that the structure of PANI-EB corresponds to the benzene ring and quinone ring units in the same proportion. Furthermore, the characteristic peaks in the doped anion region disappear completely in the doped PANI state, which indicates the success of the de-doping step and verifies the successful preparation of PANI-EB. This change is also reflected in the characteristic peak curve of PANI-EB@C.

Moreover, the Raman spectrum in Fig. 3e and Table S2 could further verify the result of FTIR. It is demonstrated that for PANI-1, PANI-2 and PANI-Re, the partial peak near the quinoid ring, the main peak of benzenoid and of C-N⁺ which are related to doping are gradually enhanced, which implies the deepening of doping degree. In the C-H and C-C vibration peaks, PANI-2 shows a great difference, which verifies that its doped anions may exist in two different forms: Cl⁻ and CCl₃⁻. Compared with doped PANI, the B characteristic peak intensity of PANI-EB is significantly decreased, and the N=Q=N characteristic peak is displayed, indicating the existence of further quantity of quinoid ring structures in the structure, suggesting the successful synthesis of the PANI-EB. In addition, it can be seen from Fig. S2 that PANI-EB@C presents a characteristic peak introduced by CNT-MW in the range of 2500-2800 cm⁻¹.

The peak data in N 1s region obtained from XPS spectra further distinguishes the differences of synthesized PANI samples from a bonding perspective. As shown in Fig. 3f, for the doped PANI-1, PANI-2, and PANI-Re, the fitting peak representing -NH⁺- continuously increases, while which of -NH- continuously decreases. This protonation transformation indicates an increase in and complexity of the doping level. In contrast, PANI-EB and PANI-EB@C almost lack the -NH⁺- fitting peak that reflects the doping level, and instead exhibit an -N= fitting peak that is almost equivalent to the -NH- fitting peak. This non-protonated N functional group reflects the dominant role of the quinone ring structure in PANI and is the main characteristic feature of emeraldine based state in PANI.

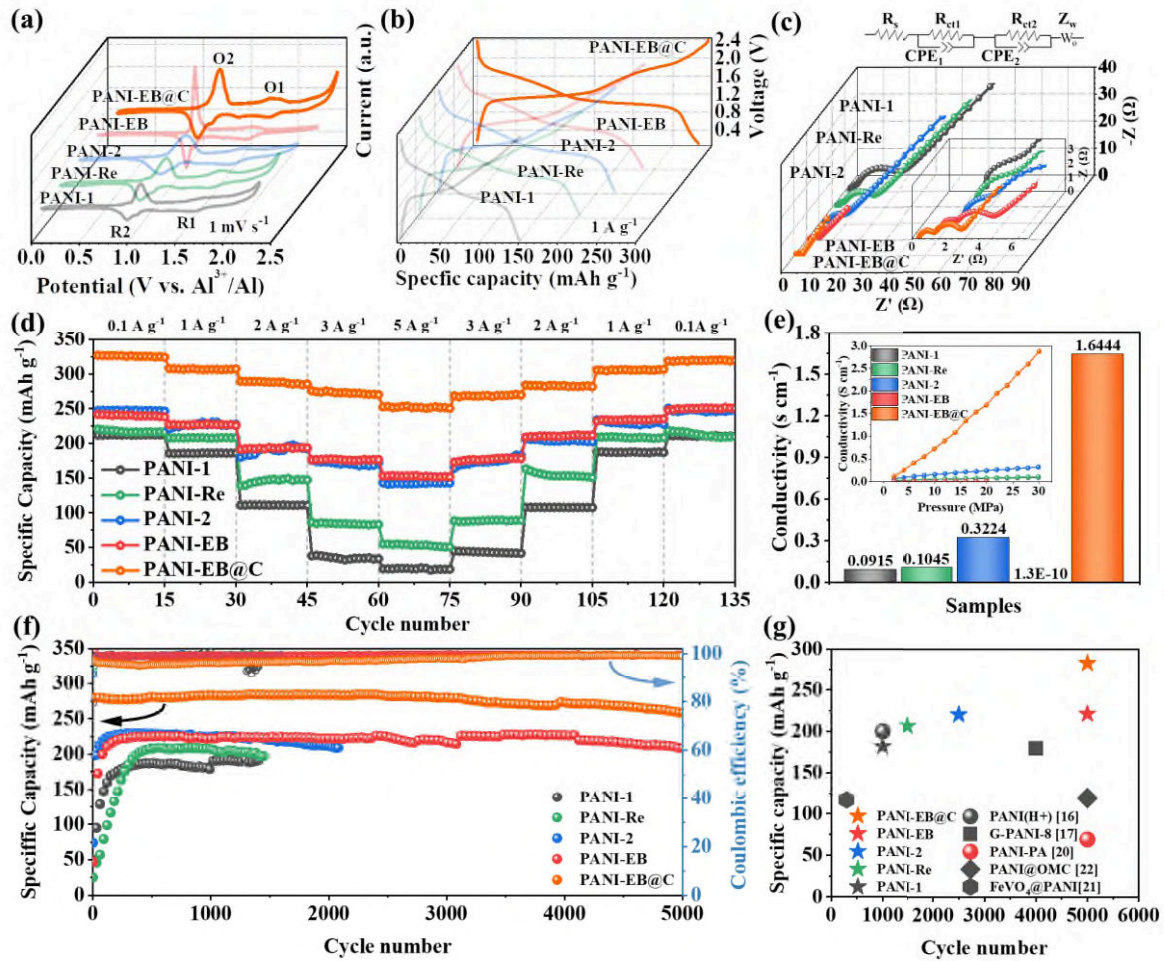


Fig. 4. Electrochemical analysis results of PANI-1, PANI-Re, PANI-2, PANI-EB, and PANI-EB@C: (a) typical CV curves within 0.1–2.4 V; (b) charge–discharge curves at current density of 1 A g⁻¹ in the voltage range of 0.1–2.4 V; (c) EIS data (Nyquist plots) after the 50th cycling at current density of 1 A g⁻¹ (d) rate performance under current density from 0.1 to 5 A g⁻¹; (e) conductivity data of samples; (f) long-term cycling performance at current density of 1 A g⁻¹ in the voltage range of 0.1–2.4 V and (g) comparison of the performance for PANI cathode materials between this work and reported ones in RAIBs [23, 24, 26, 28, 29].

The successful synthesis of PANI with different doping and emeraldine based states was validated by a variety of physicochemical results, while different electrochemical tests were employed to further distinguish the impact of different doping states on the electrode performance of PANI. From the cyclic voltammetry (CV) curves in Fig. 4a and the typical voltage platform in Fig. 4b, it can be observed that for all PANI materials, there are two pairs of distinct oxidation-reduction peaks (O_1/R_1 , O_2/R_2) around 1.7–1.8 V and 1.0–1.2 V, respectively. As the doping process becomes more complex, the potential difference between the oxidation-reduction peaks increases, implying the influence of protonation level. The three different doping states exhibit varying patterns in the oxidation-reduction behaviour. It is evident that the CV curve of PANI-EB differs significantly from that of doped PANI, with a reduced potential difference between the oxidation-reduction peaks and an improved electrode energy density. Particularly, PANI-EB@C shows a pronounced upward trend near the end at around 2.4 V, attributed to the introduction of CNT-MW. In addition, it can be seen from Fig. S3 that there is no obvious redox reaction in CV curve of CNT-MW cathode in the same battery system, which implies that it could work as a reliable frame and conductive medium without causing undue interference to PANI-EB@C cathode. Different from the introduction of CNT-MW, the rise at the high voltage of about 2.4 V for PANI-1 and PANI-Re is caused by the decomposition of small molecular acids dopant (such as HCl, while not obvious for CHCl_3 in PANI-2). During the cycling, the gas generated by decomposition causes the bulge phenomenon of the battery as shown in Fig. S6, which further weaken its cycling performance.

The results of EIS (Nyquist plots) tests and fitting the data to an equivalent circuit are shown in Fig. 4c and Table S3. In the figure, R_s represents the ohmic resistance, manifested as the first intersection point of the high-frequency data with the x-axis. R_{ct1} and CPE_1 represent the resistance of ion transport through the SEI membrane and a constant phase element, respectively, manifested as the first semicircle in the high-frequency region. R_{ct2} and CPE_2 correspond to the charge transfer resistance at the electrolyte interface, manifested as the second semicircle in the mid-frequency region. Z_w represents the diffusion resistance of ions and is located in the low-frequency region. According to the fitting results, for the doped PANI samples, the resistance values of

PANI-2 are significantly lower than those of PANI-1 and PANI-Re. This is because the first doping is at the small polaron limit with a bandgap, while the second doping is at the large polaron limit, exhibiting metallic characteristics without a bandgap, resulting in a significant improvement in conductivity [32]. Compared with PANI-EB, the lower resistance value of PANI-EB@C could be attributed to the composite with CNT-MW, leading to a significant improvement in conductivity. As the doping level becomes deeper and more complex, the conductivity of the cathode materials in RAIBs correspondingly increases, which is also validated in the conductivity tests.

The rate performance of PANI-1, PANI-Re, and PANI-2 continuously improves as the doping level of PANI becomes sufficiently complex, as shown in Fig. 4d, until it is comparable to PANI-EB at a low current density of 0.1 A g^{-1} , exhibiting discharge specific capacities of 325, 307, 287, and 273 mAh g^{-1} , and at a high current density of 5 A g^{-1} , exhibiting discharge specific capacities of 212, 218, 246, and 240 mAh g^{-1} , respectively. Notably, the discharge specific capacities of PANI-EB@C loaded with CNT-MW are 325 and 252 mAh g^{-1} at these two current densities, representing a significant enhancement in rate performance compared to PANI-EB. This improvement in performance may be attributed to the variation in the conductivity of PANI under different doping states, as doped PANI is conductive while the emeraldine based PANI is generally considered an insulator. Although the conductivity of PANI-EB itself is extremely low, it can be seen in the experimental section that the cathode still has a certain conductivity when it is prepared and assembled as RAIBs, thanks to the addition of conductive carbon. Fig. 4e illustrates that the complexity of doping is crucial for enhancing the conductivity of doped PANI, and the introduction of highly conductive CNT-MW turns PANI-EB@C into an outstanding conductive electrode material, unlike PANI-EB, achieving an order of magnitude improvement compared to PANI-2. This may be one of the key factors leading to a substantial enhancement in its electrochemical performance.

The influence of conductivity on the electrochemical performance of PANI electrodes is also reflected in the long-term cycling data in Fig. 4f, and the theoretical capacity of PANI is about 294 mAh g^{-1} . At a current

density of 1 A g^{-1} , the discharge specific capacity of PANI-1 stabilizes at 186 mAh g^{-1} but rapidly decays after 1000 cycles. A similar trend is observed for PANI-Re, which stabilizes at a discharge specific capacity of 208 mAh g^{-1} but also experiences rapid decay after 1500 cycles. This may be attributed to the presence of small-group inorganic doping acid HCl, which renders the structure of the less-doped PANI unstable. This phenomenon is somewhat mitigated in the PANI-Re electrode with more complex doping, as its specific capacity stabilizes at 225 mAh g^{-1} and exhibits significant decay only after more than 2000 cycles, with a capacity retention rate of 92.89%. In comparison to doped PANI, PANI-EB, due to the absence of acid-doped groups, exhibits a more stable structure with a discharge specific capacity of 225 mAh g^{-1} , maintaining stability over 5000 cycles. It is worth noting that as can be seen from Fig. S7, the obvious activation step of doped PANI is significantly alleviated at a lower current density and finally optimized by stable spatial structure in PANI-EB@C. Furthermore, the discharge specific capacity of PANI-EB@C is further enhanced, stabilizing at 284 mAh g^{-1} , and after 5000 cycles, the discharge specific capacity remains at 259 mAh g^{-1} , with a capacity retention rate of 91.19%. The full capacity utilization of PANI-2 and PANI-EB is 76.53%, while that of PANI-EB@C is 96.59%. As can be seen from Fig. S4, the full capacity utilization of PANI-EB@C could still reach 93.88% even if the capacity of CNT-MW itself (about 8 mAh g^{-1}) is excluded.

As can be seen from Fig. 2g, the specific discharge capacity of doped PANI is close to or even exceeds the reported level, while PANI-EB and PANI-EB@C demonstrate extremely superior electrochemical performance, which is attributed to the discrimination and cognition of the unique and diversified structure and characteristics of PANI materials.

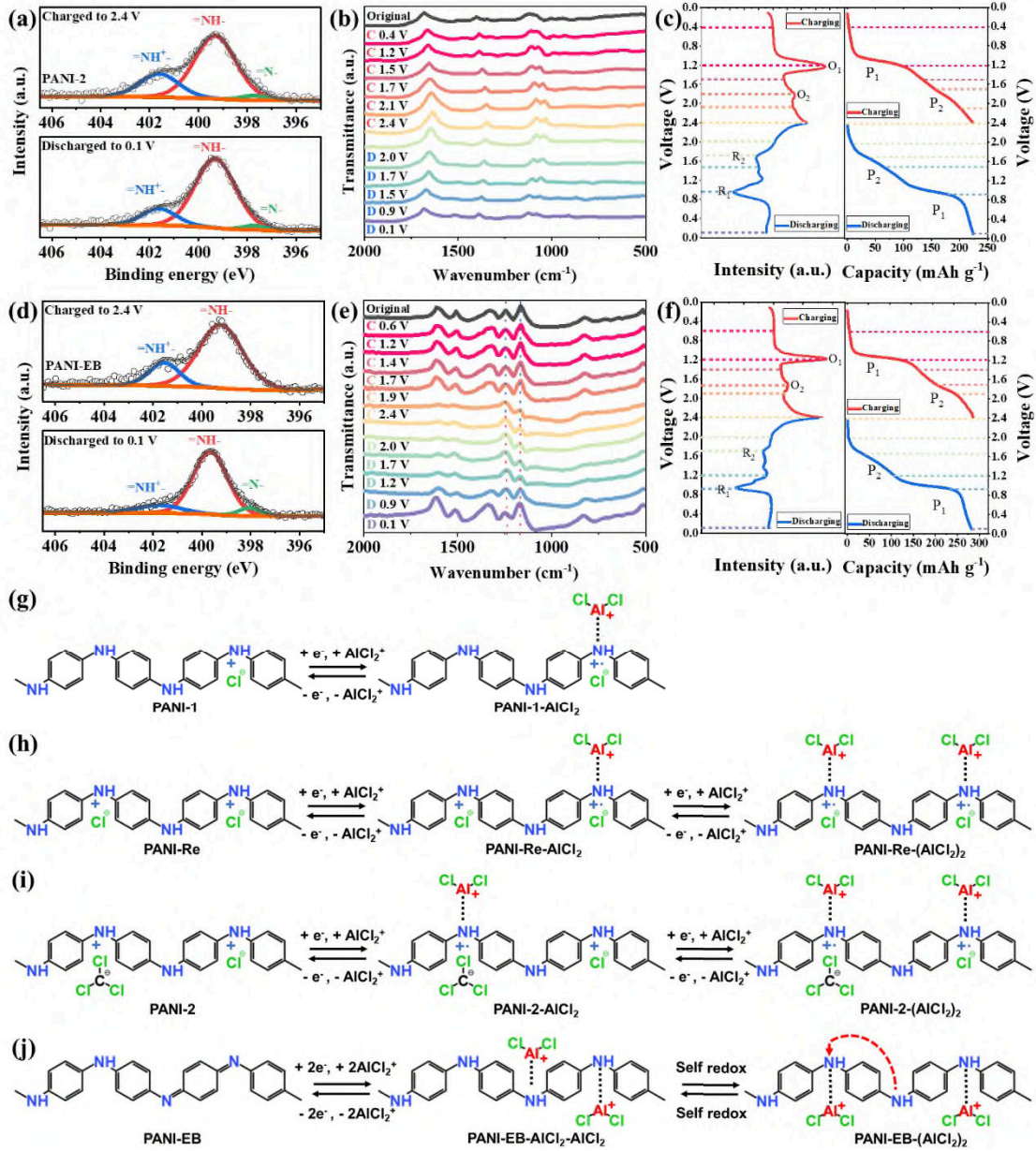


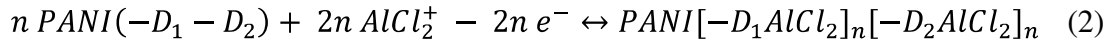
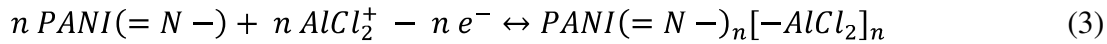
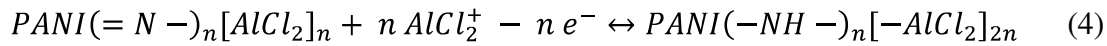
Fig. 5. N 1s XPS fits of (a) PANI-2 and (d) PANI-EB as charged to 2.4 V and discharged to 0.1 V; *ex-situ* FTIR spectra of (b) PANI-2 and (e) PANI-EB corresponding to the charge/discharge and CV curves in (c) and (f); The redox mechanism of (g) PANI-1, (h) PANI-Re, (i) PANI-2 and (j) PANI-EB.

The XPS data of PANI-2 in Fig. 5a reveals that the peak signal representing the doping group ($=NH^+$) noticeably weakens during discharge to 0.1 V and significantly strengthens upon charging to 2.4 V, while the peak signal representing the quinone ring ($=N^-$) shows almost no significant change. It implies that the cathode material could only undergo a process of separation/combination with $AlCl_2^+$ ions during the charge-discharge process. This was further validated by the *ex-situ* FTIR data in Fig. 5b and corresponding performance in Fig. 5c, where only the characteristic peak intensity representing the doped group undergoes noticeable enhancement and weakening during the charge-discharge reaction. While the phenomenon of blue-shift and red-shift suggests that the molecular chain of the doped PANI is more obviously affected by the sole combination/separation of $AlCl_2^+$ in the process of charge and discharge, which is quite different from the multiple effects in PANI-EB.

The XPS data in Fig. 5d, the *ex-situ* FTIR data in Fig. 5e and corresponding performance in Fig. 5f reveal that during discharge to 0.1 V, the signal representing the $=N^-$ group of quinone ring is noticeably present, while upon charging to 2.4 V, this signal essentially disappears. Concurrently, the signal representing the doped $=NH^+$ group significantly strengthens, indicating that the cathode material undergoes simultaneous internal redox reactions (interconversion between the benzene and quinone rings) and combination/separation of $AlCl_2^+$ ions during the charge-discharge process. During this process, PANI-EB gradually combines/separates a large amount of $AlCl_2^+$, contributing a substantial amount of battery capacity. Additionally, in the charging range of 1.9–2.4 V and discharging range of 2.0–1.2 V, the intensity ratio of the quinone/benzene characteristic peaks changes from high-quinone/low-benzene, to roughly equal, and then shifts to high-benzene/low-quinone. This indicates a significant amount of quinone-to-benzene and vice versa transformation, reflecting the internal redox

reactions of PANI-EB, corresponding to the second pair of redox peaks(O_2/R_2) and the charge-discharge plateau (P_2), contributing to an additional battery capacity.

Based on the experimental and characterization results above, it is proposed that the working mechanism of PANI-based cathodes in RAIBs could be described as two processes in terms of the two different specific doping states. As shown in Fig. 5g-i, doped PANI undergoes combination/separation of $AlCl_2^+$ at the N sites where the doping acid is bound, involving a simple doping process (with single dopant D_1) as depicted in **Equation 1** and a complex doping process (with different dopants D_1 and D_2) as shown in **Equation 2**, accompanied by electron gain and loss. As shown in Fig. 5j, intrinsic PANI undergoes combination/separation of $AlCl_2^+$ at the N sites of the quinone ring (**Equation 3**), concurrent with internal redox reactions (**Equation 4**) and accompanied by electron gain and loss. The same reaction at the anode (**Equation 5**) should involve the interconversion between $Al_2Cl_7^-$ and $AlCl_4^-$ to generate $AlCl_2^+$ (**Equation 6**).



3. Conclusion

In summary, to fully achieve the theoretical capacity (294 mAh g^{-1}) of PANI organic cathode materials, we conducted in-depth research on the structure-performance relationship of different doping forms of PANI, including PANI-1, PANI-Re, PANI-2, and PANI-EB. In particular, we prepared the enhanced conductivity PANI-EB@C composite by using CNT-MW, the latter of which has been less studied. Through electrochemical analysis, Gaussian calculations, and *ex-situ* characterization, we verified the performance and reaction mechanisms of these cathode materials. Among them, under the conditions of doping state, the conductivity of PANI-1, PANI-Re, and PANI-2 increased with the complexity of dopant, and the electrochemical performance gradually improved. At a current density of 1 A g^{-1} , the specific capacity is 225 mAh g^{-1} (full capacity utilization rate of 76.53%), and the capacity retention rate was 92.89% after 2000 cycles. Meanwhile, the discharge specific capacity of PANI-EB@C with a unique internal redox mechanism reaches 284 mAh g^{-1} (full capacity utilization rate of 96.59%), with a capacity retention rate of 91.19% after 5000 cycles. Its performance not only surpasses all previously reported PANI in RAIBs, but also significantly outperforms other common organic cathode materials. This work not only demonstrates that PANI-EB is the most advantageous form of PANI as a cathode material, but also provides important insights into the structural characteristics and charge-discharge mechanisms of PANI, representing a promising direction for the development of high-performance RAIBs in the future.

CRediT authorship contribution

Guokang Wei: Conceptualization, Data curation, Investigation, Writing-Original draft preparation.

Jia Qiao: Conceptualization, Writing-reviewing and editing, Supervision, Project administration.

Xin Li: Formal analysis, Methodology.

378 Fei Tao: Resource, Validation.
379 Weixi Xue: Data curation, Investigation.
380 Sijiang Hu: Data curation, Methodology.
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382 Jianhong Yang: Supervision, Writing-reviewing and editing.

383 **Declaration of competing interest**

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

386 **Data availability**

387 Data will be made available on request.

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