

Effects of Different Acids Dopant on the Electrochemical Properties of Polyaniline Cathode in Aluminum-ion batteries

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Abstract. Polyaniline (PANI) as the cathode material has caused great concern in aluminum-ion batteries (AIBs) due to the low cost of raw materials, simple synthesis, good chemical stability and electrochemical reversibility. However, the effect of different doping acids on the electrochemical performance of PANI cathode has not been investigated. Here we preparation of PANI by use strong acids, medium-strong acids and weak acid as dopants. Results show that the specific capacity of PANI doped with strong acids is up to 180 mAhg⁻¹ at the current density of 100 mA g⁻¹, which is much higher in comparison with those doped with medium-strong acids (100-120 mAhg⁻¹) and weak acid (<60 mAhg⁻¹). The electrochemical properties of PANI electrode materials are mainly affected by its crystallinity, doping degree, conductivity and morphology.

Keywords: Polyaniline, Acid dopant, Aluminum-ion batteries.

1. Introduction

Aluminum-ion batteries (AIBs) are a type of very promising energy storage device due to their high capacity, high charge transfer efficiency, low cost, and high safety. [1-2] The key to the research of AIBs is the cathode material. Up to now, there are basically two types of materials intensively investigated. One is the graphitic materials, [3] which present a limited capacity in storing large-size AlCl₄⁻ anions (0.528 nm) [4] into the graphitic interlayer space. This characteristic makes it difficult to further improve their capacity, which is usually lower than 120 mAhg⁻¹. The other is metal dichalcogenides, [5] which initial discharge capacities are significantly high, reaching up to 300-500 mAhg⁻¹, but their cycle stability is rather poor. Their capacity usually decreases to about 100 mAhg⁻¹ or lower values after 100-500 cycles.

Therefore, cathode materials with a higher capacity and stable performances are required. Conductive polymers [6] are an important class of electrode materials for metal-ion batteries due to their high theoretical specific capacity, rapid and reversible redox reactions in their entire three-dimensional bulk phase. Among the conducting polymers, polyaniline (PANI) has been favored due to its low cost of raw materials, facile synthesis, good chemical stability and electrochemical reversibility. [7,8] In the process of preparing PANI by a simple chemical oxidation method, the doped of the acid is the key to the transformation of PANI from insulating state to conducting state [9]. However, the effects of crystallinity, conductivity and microstructural differences on the electrochemical performance of PANI doped with different acids have not been systematically investigated.

In this work, the oxidative polymerization method was used to prepare PANI with strong acids (hydrochloric acid and Methanesulfonic acid), medium-strong acids (Tartaric acid, Citric Acid and Hydrofluoric acid) and weak acid (Formic acid) as dopants respectively. The electrochemical behavior of PANI was systematically studied, and the fundamental reasons for there performance difference were explored by X-ray diffraction (XRD), Raman, Powder resistivity instrument, scanning electron microscope(SEM) and other methods.

2. Experiment section

2.1. Reagents and apparatus

Aniline, Hydrochloric acid (HCl), Methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$), Tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$), Citric Acid ($\text{C}_6\text{H}_8\text{O}_7$), Hydrofluoric acid (HF), Formic acid (HCOOH) and Ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) were purchased from Aladdin Chemicals Reagent Co., Ltd. (Shanghai, China). All the reagents were of analytical grade and used as received. All solutions were prepared with ultrapure water.

The sample crystal structures were analyzed via powder X-ray diffraction measurements (XRD, D8 Advance, Bruker, Germany) by using the $\text{CuK}\alpha$ radiation at 40 kV and 30 mA. The Raman spectra were recorded by using a 532 nm-laser excitation at room temperature (HORIBA HR Evolution). The microscopic morphology and the microstructure of the samples were observed via field-emission scanning electron microscopy (SEM, Sirion 200, FEI, Netherlands). The conductivity of powder samples was measured by powder resistivity instrument (SZT-D, ST2253, China) under the pressure of 40 MPa.

2.2. Preparation of PANI with different acid doping materials (AD-PANIs).

A certain amount of acid was added to a certain amount of water and mixed evenly, and configured into 1 mol/L acid solution. 41.7 mL acid solution was stirred at 0 °C for 30 min. Afterwards, a quantity of 0.8 mL of aniline and 8.3 mL of ammonium persulfate solution were added to the mixture and stirred vigorously for 24 h at 0 °C. The suspension was then aged at 85 °C for 72 h. The obtained product was filtered through a polyester fiber (Carpenter Co.) and washed with deionized water several times to remove the impurities. The wet product was then lyophilized and the dried compound was designated as x-PANI, where x represents type of acid dopant. The PANI doped with hydrochloric acid (HCl), Methanesulfonic acid (MSA), Tartaric acid (TA), Citric Acid (CA), Hydrofluoric acid (HF) and Formic acid (FA) are named HCL-PANI, MSA-PANI, TA-PANI, CA-PANI, HF-PANI and FA-PANI respectively.

2.3. Fabrication of the electrochemical cell.

The samples were ground with acetylene black and polyvinylidene fluoride (PVDF) with a mass ratio of 6:3:1 to prepare the cathodes. After adding methylpyrrolidone as the dispersing agent, the mixture was coated onto a rounded molybdenum current collector of 12 mm diameter, which was dried at 80 °C in vacuum for 12 h. The amount of the active material loaded was in the range of 1.5-2 mg. An aluminum foil (99.99%) was used as the anode component. The AIBs were assembled by using a customized Swagelok-type cell in an argon-filled glove box at room temperature. One piece of glass fiber paper (Whatman 934-AH) was placed between the Al anode and the cathode. A quantity of 80 μL of ionic liquid electrolyte was added to the cell to wet the separator. The preparation method of ionic liquid electrolyte is consistent with the previous literature. [7]

2.4. Electrochemical measurements.

The galvanostatic charge/discharge measurements were performed on a LANHE battery tester. Cyclic Voltammetry (CV) measurements were conducted with different scan rates over a range of 0.1-2.3 V versus $\text{Al}/\text{AlCl}_4^-$ on an electrochemical workstation (CHI 660E, Chenhua Instrument Corporation, China) using a three electrode mode, where the reference electrode and the counter electrode was constituted of an Al foil, and the working electrode of the samples, which were coated on a Mo foil.

3. Results

The structure, crystallinity and doping degree of the six doped PANIs were characterized by X-ray powder diffraction (XRD) analysis and Raman spectroscopy. For the Raman spectrum of AD-

PANI (Fig. 1a), five new typical peaks (*) generated by PANI can be found at 800, 1165, 1400, 1471-1505 cm^{-1} and 1590 cm^{-1} , which correspond to substituted benzene ring deformation, C-H bending of the quinoid ring, C-N stretching, C=N stretching of the quinoid ring and C-C stretching of the benzoid, respectively. [10,11] In addition, The peak at 1218 cm^{-1} is attributed to the stretching vibration of the C-N single bond, and the characteristic peak between 1300 cm^{-1} and 1370 cm^{-1} corresponds to the C-N⁺ stretching vibration (#) of the delocalized polaron charge carrier, which indicates that PANI is in the doped state. [12]

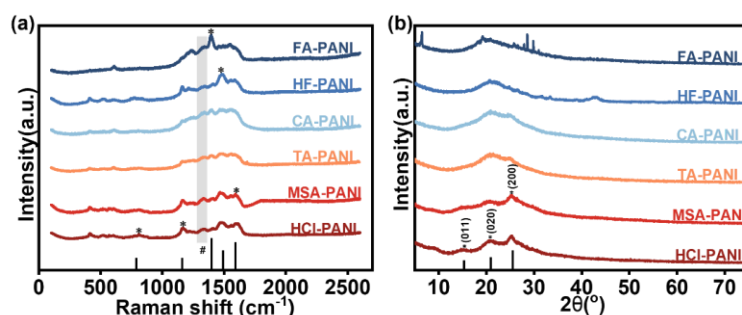


Figure 1. (a) Raman spectra and (b) XRD pattern of AD-PANI

As shown in Fig. 1b, the XRD pattern of the AD-PANIs shows three features at $2\theta = 15.3^\circ$, 20.9° and 25.5° , which correspond to the (011), (020), and (200) crystal planes of PANI, respectively. [13] The peak at 15.3° is assigned to the spacing between the main chains of PANIs and the peaks at 20.9° and 25.5° correspond to the growth of PANI parallel and perpendicular to the chain direction, respectively. Here, it is found that compared with other PANIs, HCl-PANI and MSA-PANI exhibits an enhanced intensity of the peak at 15.3° and 25.5° . It was proved that HCl and MSA doped PANI have the best crystallinity [14], TA-PANI and CA-PANI followed, HF-PANI and FA-PANI have the weakest crystallinity. In addition, all PANIs have obvious peaks at 20.9° , indicating that acid doping is beneficial to the orderly arrangement of PANI molecular chains along the direction parallel to the chain length. However, only HCl-PANI and MSA-PANI exhibits an enhanced intensity of the peak at 25° , suggesting that doping of HCl and MSA may also facilitate the growth of PANI perpendicular to the chain direction. [15] This may effectively improve the conductivity and charge transfer rate of the materials, thereby effectively improving the rate performance and specific capacity of the cathode.

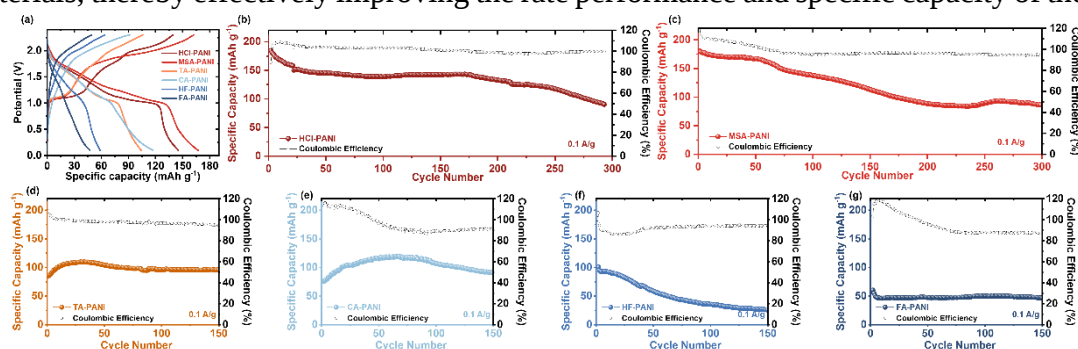


Figure 2. (a) typical Charge/discharge voltage profiles of AD-PANIs at a current density of 100 mA g^{-1} after 50 cycles; the cycling performance and the coulombic efficiency of (b) HCl-PANI, (c) MSA-PANI, (d) TA-PANI, (e) CA-PANI, (f) HF-PANI and (g) FA-PANI cathode at a current density of 100 mA g^{-1} with the cut-off voltage of 2.3 V

To explore the effect of different acid dopants on the electrochemical performance of PANI in AIBs, its electrochemical performance as a cathode material was evaluated in an AIB cell. Fig. 2a shows the galvanostatic charge-discharge curves of the six doped PANIs at a current density of 100 mA g^{-1} after circulation stabilization (50 cycles). Obviously, there are a long and glossy voltage plateau (~ 1.0 - 2.0 V vs $\text{Al}/\text{AlCl}_4^-$) in the charge process and a declined plateau (2.0 - 1.0 V vs $\text{Al}/\text{AlCl}_4^-$) in the discharge process, indicating that AD-PANIs cathodes can store energy in AIBs, but the specific capacity and platform of HCl-PANI and MSA-PANI electrodes are significantly better than

other acid-doped PANIs, followed by TA-PANI and CA-PANI, the specific capacity of HF-PANI is lower, and FA-PANI even has no obvious platform, which proved that the stronger of the acid, the higher specific capacity of the doped PANI. It can also be seen from the cycling performance of the PANI electrodes doped with different acids in Fig. 2b-g that the strong acid has high initial specific capacity (HCl-PANI is up to 184 mAhg^{-1} , MSA-PANI is up to 180 mAhg^{-1} at 100 mA g^{-1}) and good cycle stability, of which HCl-PANI is the best, the discharge capacity retention rate is 72% after 200 cycles, which may be due to the more suitable structure of HCl-PANI.

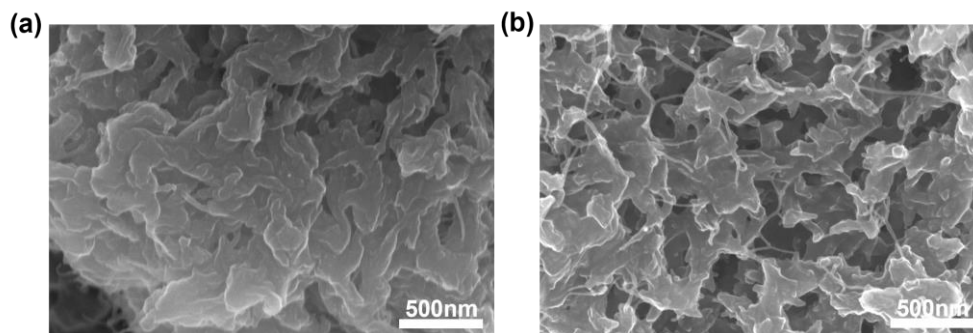


Figure 3. SEM image of (a) HCl-PANI and (b) MSA-PANI

As shown in Fig. 3, MSA-PANI presents a sheet-like stacking structure with some holes, which makes the higher initial capacity, even surpassing the specific of HCl-PANI after 5 cycles. However, the porous structure is easy to collapse, resulting in poor cyclic stability. While the HCl-PANI presents a short-rod-like structure, which takes into account both the exposure of active sites and the stability of the structure, showing good specific capacity and cyclic stability.

Compared with strong acid doped PANI, the cyclic stability of organic medium-strong acid doped PANI is good, but the capacity is relatively low, the TA-PANI is up to 109 mAhg^{-1} (Fig. 2d) and the CA-PANI is up to 119 mAhg^{-1} at 100 mA g^{-1} (Fig. 2e). It is worth noting that the cycle capacity curves of AIBs cathode materials obtained by de-doping PANI with polyhydroxycarboxylic acid molecules such as TA and CA have a common feature is that the capacity needs to have an activation process in the first few cycles, and then the capacity tends to be stable. The reason for this phenomenon is that the carboxylate anions with strong polar groups in the doping process will lead to enhanced interactions between polyaniline molecular chains and PANI molecules tend to agglomerate [16], and the internal PANI molecules could not effectively adsorb AlCl_4^- in the early cycle due to the diffusion. which led to the low capacity in the initial cycle. In addition, although the weak acid (FA-PANI) has strong capacity retention ability, its specific capacity is less than 60 mAhg^{-1} after stabilization, and its Coulombic efficiency during the cycle is also unsatisfactory.

Table 1. Conductivity comparison between AD-PANI (P=40MPa)

	HCl-PANI	MSA-PANI	TA-PANI	CA-PANI	HF-PANI	FA-PANI
Resistivity ($\Omega \cdot \text{cm}^{-1}$)	161.68	130.35	196.18	192.08	495.60	568.65

Combined with the previous XRD characterization, it is not difficult to conclude that the strong acid-doped PANIs has better electrochemical performance because they have better crystallinity and conjugate length in both parallel and vertical molecular chain directions, which can effectively improve the conductivity and charge transfer rate of the materials [15] the Nyquist plots (Fig. 4a) and conductivity test (Table 1) also proved this. Powder conductivity test revealed that the electrical conductivity of MSA-PANI and HCl-PANI is apparently higher than other acid doped PANIs. As shown in Figure 4a, the Nyquist plots of AD-PANI consist of a suppressed semicircle at high frequency and an inclined line at low frequency. Usually, smaller diameter of the semicircle means lower charge transfer resistance (R_{ct}), and higher slope of the inclined line refers to lower Warburg resistance (R_w). It is obvious that MSA-PANI and HCl-PANI exhibits relatively lower R_{ct} and R_w compared with other PANIs, demonstrating that the doping of MSA and HCl can provide a more easier transfer of electrons and electrolyte ions at the PANI–electrolyte interface. Moreover, the

kinetics of PANI can be further explored by the cyclic voltammograms (CV) curve of HCl-PANI (Fig. 4b). The anodic and cathodic peaks gradually shift toward slightly positive and negative potentials, respectively, as the scan rate increases, indicating a weak polarization. These observations reveal that these redox reactions have an excellent kinetics. The relation between the peak current and the scan rates can be expressed via the following equations:

$$i = av^b \quad (1)$$

$$\log(i) = \log(a) + b\log(v) \quad (2)$$

where i is the response current (in mA) and v is the scan rate (in mV s^{-1}); a and b are adjustable values. As the inset in Fig. 4b shows, the parameter b is close to a value of 0.51, indicating that the fast kinetics of PNA electrodes in AIBs are mainly dominated by diffusion-controlled. [16]

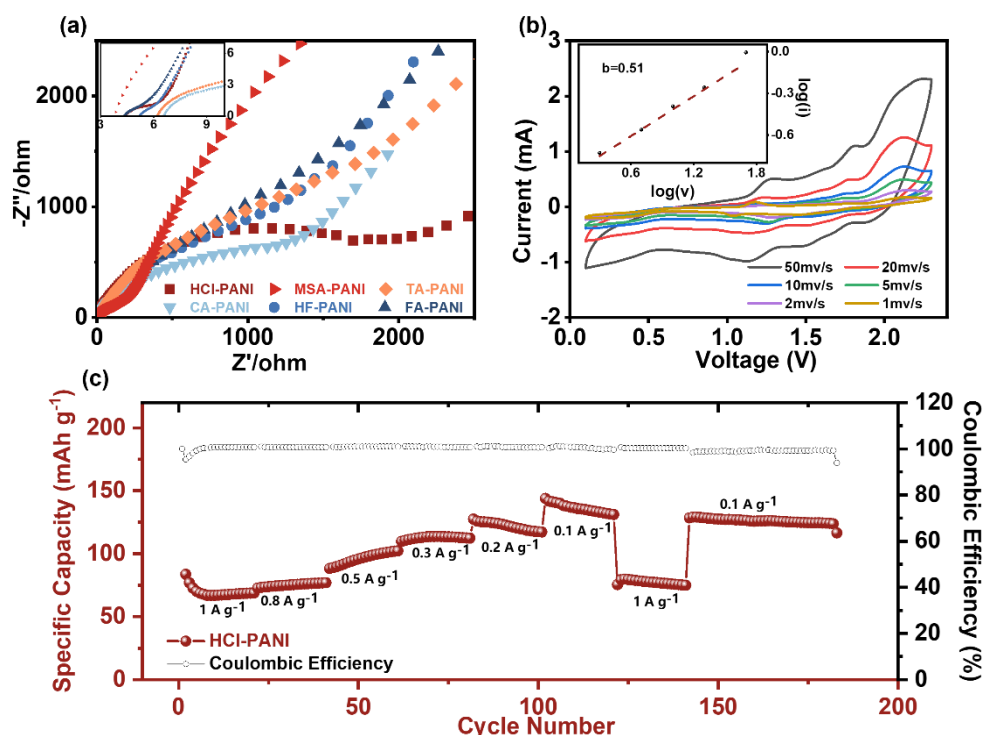


Figure 4. (a) Nyquist plots for the AD-PANI cathodes (the inset is the enlarged view of the high frequency region); (b) Typical CV curves of HCl-PANI cathode at various scan rates from 1 to 50 mV s^{-1} ; the inset shows the relation between the current and the scan rate; (c) specific capacities and coulombic efficiencies of HCl-PANI cathode at different current density from 100 mA g^{-1} to 1000 mA g^{-1}

Such excellent kinetics and low charge transfer resistance are the result of the good rate capability of HCl-PANI (Fig. 4c), as the current density dropped from 1 A g^{-1} to 100 mA g^{-1} , the specific capacity of the HCl-PANI cathode only decreases of by 40%, when the current density is adjusted back to 1 A g^{-1} , its capacity can still be maintained at 130 mAh g^{-1} .

4. Conclusions

In summary, when strong acid-doped PANIs are used as the cathode materials of AIBs, the specific capacity can reach 180 mAh g^{-1} at 0.1 A g^{-1} , and the specific capacity retention rate of HCl-PANI can be maintained at 72% after 200 cycles, the electrochemical performance is better than that of PANI doped with medium-strong acid and weak acid under the same conditions. AD-PANI has differences in crystallinity, doping degree, resistivity and morphology. The higher crystallinity and doping degree, smaller resistivity, and the stable structure result in better electrochemical performance.

Acknowledgements

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References

- [1] Armand M, Tarascon JM. Building Better Batteries. *Nature*, 2008, 451: 652-657.
- [2] Elia GA, Marquardt K, Hoeppe K, et al. An Overview and Future Perspectives of Aluminum Batteries. *Advanced Materials*, 2016, 28(35): 7564-7579.
- [3] Xu J, Dou Y, Wei Z, et al. Recent Progress in Graphite Intercalation Compounds for Rechargeable Metal (Li, Na, K, Al)-Ion Batteries. *Advanced Science*, 2017, 4(10): 1700146.
- [4] Jung S C, Kang Y J, Yoo D J, et al. Flexible Few-Layered Graphene for the Ultrafast Rechargeable Aluminum-Ion Battery. *Journal of Physical Chemistry C*, 2016, 120(25): 13384-13389.
- [5] Zhang Y, Liu S, Ji Y, et al. Emerging Nonaqueous Aluminum-ion Batteries: Challenges, Status, and Perspectives. *Advanced Materials*, 2018, 30(38): 1706310.
- [6] Xie J, Zhang Q, et al. Recent Progress in Multivalent Metal (Mg, Zn, Ca, and Al) and Metal-Ion Rechargeable Batteries with Organic Materials as Promising Electrodes. *Small*, 2019, 15(15): 1805061.
- [7] Wang D, Hu H, Liao Y, et al. High performance aluminum-polyaniline battery based on the interaction between aluminum-ion and -NH groups. *Science China-Materials*, 2020, 62: 318-328.
- [8] Liao Y, Wang D, Li X, et al. High performance aluminum ion battery using polyaniline/ordered mesoporous carbon composite. *Journal of Power Sources*, 2020, 477: 228702.
- [9] Abdolahi A, Hamzah E, Ibrahim Z, et al. Synthesis of Uniform Polyaniline Nanofibers through Interfacial Polymerization. *Materials*, 2012, 5(8): 1487-1494.
- [10] Yan X, Chen J, Yang J, et al. Fabrication of Free-Standing, Electrochemically Active, and Biocompatible Graphene Oxide Polyaniline and Graphene Polyaniline Hybrid Papers. *Acs Appl Mater Interfaces*, 2010, 2(9): 2521-2529.
- [11] Wang H, Hao Q, Yang X, et al. Effect of Graphene Oxide on the Properties of Its Composite with Polyaniline. *Acs Appl Mater Interfaces*, 2010, 2(3): 821-828.
- [12] Tagowska M, Pałys B, Jackowska K. Polyaniline nanotubules-anion effect on conformation and oxidation state of polyaniline studied by raman spectroscopy. *Synthetic Metals*, 2004, 142: 223-229.
- [13] Yan J, Tong W, Bo S, et al. Preparation of a graphene nanosheet/polyaniline composite with high specific capacitance. *Carbon*, 2010, 48(2): 487-493.
- [14] Chen S A, Lee H T. Polyaniline plasticized with 1-methyl-2-pyrrolidone: Structure and doping behavior. *Macromol*, 1993, 26(13): 3254-3261.
- [15] Zhang L, Zhang L, Wan M, et al. Polyaniline micro/nanofibers doped with saturation fatty acids. *Synthetic Metals*, 2006, 156: 454-458.
- [16] Philip D; Stoddart JF. Self-Assembly in Natural and Unnatural Systems. *Angewandte Chemie International Edition*, 1996, 35(11): 1154-1196.
- [17] Ren W, Zhu Z, Qin M, et al. Prussian White Hierarchical Nanotubes with Surface-Controlled Charge Storage for Sodium-Ion Batteries. *Advanced Functional Materials*, 2019, 29(15): 1806405.