A review of polyaniline based materials as anodes for lithium-ion batteries

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Abstract. Conducting polyaniline is of great research interest to use as anode material for lithium-ion batteries. However, the development of polyaniline still remains significant challenges. For example, nowadays, it is not easy to effectively improve the electrochemical performance of ions batteries and promote its application. Herein, we introduce the structure, synthesis and properties of polyaniline firstly, then we summarize the recent advances and applications of PANI based hybrid materials in anodes for lithium-ion batteries. Special attentions were given on the following items: carbon-polyaniline composite, silicon-polyaniline composite, and metal oxides-polyaniline composite. The superior chemical nature of polyaniline enables it is promising to use as advanced anode material for Lithium-ion batteries.

1. Introduction
For modern society in the 21st century, reliance on fossil fuels has long been refuted for the deterioration of energy crisis as well as environmental issues, two major problems for the survival of human beings, which promotes the popularization of clean energy source including solar, wind and water power. [1] Furthermore, the development and innovation of alternatives for fossil fuels are advocated worldwide, resulting the discoveries of new types of renewable energy source.

Chemical power hence takes place in the replacement of high-polluting fossil fuels in developed countries, as a possible trend of development of clean energy source. Lead acid cells, nickel hydrogen cells and nickel cadmium cells are first suggested but finally eliminated due to the negative impact on environment because of heavy metals. After the invention by M.S.Whittingham in 1970s, lithium and lithium ion cells soon dominate the field of high-performance chemical power, utilizing in various mobile devices, such as computers, cellphones, cameras, tablet computers, and music players, and even aeronautics, transportation and military, because of their excellence in high potential difference, possibility of large current, small volume, low weight, high specific capacity, little pollution, long life expectancy, and steady discharging process. [2]

Polyaniline (PANI), a polymer derived from polymerization of aniline, has specific electrical and optical properties depending on the extent of oxidation, which forms five individual structures, leucoemeraldine, protoemeraldine, emeraldine, nigraniline, and pernigraniline (Figure 1). [3] Despite its cheap price, high stability with heat and redox process, polyaniline fails to satisfy the requirements of machinability and electrical conductivity. However, doping process enables the modification of the properties of polyaniline. Each structure of polyaniline can undergo doping, including protonic acid doping mostly on imine nitrogen, photo-induced doping, ion implantation doping and electrochemical...
doping, in order to possess significant electrical conductivity and electrochemical properties. Recent researches target mostly on the synthesis of anode with polyaniline for lithium ion batteries. This essay will introduce the structure, synthesis and properties of polyaniline firstly, and then review the recent progress of PANI based materials in anode electrodes for lithium ion cells.

2. Structure, synthesis and properties of polyaniline

2.1. Structure

The conjugated structure for this polymer determines its likelihood of going through reversible redox reaction, which explains the conductivity of doped polyaniline. Doping process commonly enables the redistribution of delocalized electrons, constructing a new conjugated π ring, which is responsible to the significant boost in conductivity, for above eight orders of magnitude.

Thus, doped polyaniline recently gains increasing attention for various applications in lithium cells, especially secondary cells, mainly consisting the cathode as well as the active material, due to its low density, high stability with oxidation and water, electrical conductivity, reversibility of oxidation and reduction, and excellent ability of storing charges, which ensures low weight, high energy density, large potential difference, good cycle performance, high coulomb efficiency and possibility of recharging from its reversibility, and soon becomes a frontier research, providing plentiful experiments, theories and attempts based on the general topic of doped polymer cells.

In 1991, Japanese Bridgestone Company first promoted commercial polyaniline lithium cells, and in 1990s, the default of flammable, combustible and dry material was improved with the replacement of lithium anode with lithium implanted carbon anode. This kind of commercial polyaniline lithium cells can achieve a charge-discharge density of 800Ah/kg to 1000Ah/kg, settling the deficient of mass energy density, which leads to the same market share with nickel hydrogen cells and nickel cadmium cells. Furthermore, Kitani found when electrochemically synthesized polyaniline lithium cells are charged and discharged at 1mA/cm² between 1.0 ~ 1.7V, the charge-discharge efficiency can reach 100, the charge-discharge capacity can achieve 40Ah/kg, and the cycle life expectancy can last for over 2000 times. Meanwhile, when solid lithium cells with chemically synthesized polyaniline cathode are charged and discharged between 2.0 to 4.5V charge-discharge efficiency can reach 95 and cycle life expectancy can last for over 200 times. In addition, there are also studies targeting the secondary lithium cells consisted by compounded material of polyaniline and wax, the charge-discharge capacity can reach 120Ah/kg, and cycle life expectancy can last for over 200 times. Most polyaniline lithium secondary cells can achieve significant coulomb efficiency of over 95%.

![Figure 1. Oxidation–reduction reaction of PANI.](image)

2.2. Synthesis

Protonic acid doping process of polyaniline mainly undergoes chemical doping, which involves the protonation of imine nitrogen first and intramolecular redox reaction followed, that leads to the transferring of proton to the main chain in order to open its quinone ring. The charges on the imine nitrogen delocalize to its neighboring benzene ring or its para-nitrogen, equalizing the chemical
properties within the molecule, creating a large open π ring due to its conjugated structure. Thus, the electrical conductivity and further electrochemical properties are gained for protonic acid doped polyaniline.

The synthesis of protonic acid doped polyaniline involves reactants of aniline after reduced pressure distillation and various protonic acid, primarily including concentrated hydrochloric acid (HCl), concentrated sulfuric acid (H₂SO₄), perchloric acid (HClO₄), benzoic acid, para-methylbenzene sulfuric acid, and dodecyl benzene sulfonic acid (DBSA), where all protonic acid used are analytically pure. The widely used oxidizing agent are potassium dichromate (K₂Cr₂O₇), ammonium persulfate((NH₄)₂S₂O₈), potassium chloride (KClO₃), and Iron(III)chloride (FeCl₃). Oxidizing agents were then added into the solution by drops while stirring for about thirty minutes, and this oxidation polymerization process commonly lasted for several hours, either in room temperature or in ice-water bath, according to Zhu Yong’s approach. The product after filtration and bath with protonic acid solution, acetone and water was then protonic acid doped polyaniline.

2.3. Properties
Percentage yield or yield of the product, protonic acid doped polyaniline was calculated or measured. The conductivity of protonic acid doped polyaniline was directly measured by using four-point probe instrument, after tableting of the product under pressure of 10MPa for Yong Zhu’s team. The conductivity of polyaniline in its eigenstate is poor, at 1.71×10⁻⁹s/cm², characterized as insulator. However, after protonic acid doping process, its conductivity arises for above eight orders of magnitude, supporting by results from three distinct teams.

| protonic acid                  | pH value | yield/(g) | conductivity/(s·cm⁻¹) |
|-------------------------------|----------|-----------|----------------------|
| hydrochloric acid (HCl)       | 0        | 8.1290    | 7.482×10⁻³            |
| sulfuric acid (H₂SO₄)          | 0        | 9.5804    | 1.567×10⁻⁸            |
| salicylic acid                | 1        | 6.6798    | 1.917×10⁻⁸            |
| benzoic acid                  | 2.65     | 12.5733   | 1.411×10⁻³            |
| citric acid                   | 1.94     | 13.9489   | 7.502×10⁻⁴            |
| pyrogallic acid               | 3.73     | 3.0816    | insulator             |
| oxalic acid                   | 1.17     | 7.9825    | 2.615×10⁻³            |
| trichloroacetic acid (TCA)    | 17.9682  |           | 2.623×10⁻³            |

Certain trend relating to the properties of various protonic acid and the conductivity of protonic acid doped polyaniline can be concluded, as for inorganic protonic acids, stronger acidity of a protonic acid results in higher conductivity for the product, and higher yield as well, while lower acidity results in lower conductivity and lower yield as well, according to Yong Zhu’s results. Theorized explanation indicates that polarization process initialize in head-to-tail way under a strong acidic circumstance, where the structure and arrangement of molecular chains favor the delocalization and transition of electrons. Meanwhile, under a low acidic circumstance, aniline is then polarized in either ways of head-to-tail or head-to-head, leading to a decrease in the yield. Specifically, the dopant sulfuric acid with injection of sulfur-oxygen double bond significantly facilitates the formation of large conjugated structure that enabling the transition of electrons throughout the molecule, which proves the larger conductivity of sulfuric acid doped polyaniline comparing to other products. On the other hand, organic protonic acids doping achieves high conductivity but relativity low yield comparing to inorganic protonic acid doping. Para-methylbenzene sulfonic acid doped polyaniline, in particular, gains an overall highest conductivity, where its influence to anions lowers the interaction between aniline molecules, forcing their structures be extended, which also favors the delocalization and transition of electrons.
3. Polyaniline as anodes for Li-ion batteries

3.1. Carbon-polyaniline composite anodes
Tremendous attention was paid to improve the capacity of carbon-based anodes through functionalization strategy or surface modification of PANI materials. Hu et al. [4] reported the fabrication of multi-walled CNTs (MCNTs)-PANI- [PMo12O40]3- nanocomposites to use as the anode electrode material for Li-ion batteries. For this ternary composite, the interaction between MCNTs and H2PMo12O40 can be strengthened by the PANI layer, which was in-situ polymerized on the surface of MCNTs by π–π interactions (Figure 2). In addition, the conductive PANI can also enhance the chemical reactivity and electronic conductivity because of the protonation of PANI. In this regard, the MCNTs-PANI-[PMo12O40]3- ternary nanocomposite anode exhibited high reversible discharge capacity up to 1000 mAh g−1 at 0.5 mA cm−2 and good cycling performance for 100 cycles. Ge et al. [5] prepared the hybrid aerogel to use as flexible and freestanding electrode without using any binder or conductive agent. The aerogel consists of three-dimensional (3D) interconnected single-walled CNTs (SCNTs) and PANI. The hybrid aerogel (67 wt% PANI) shown high discharge capacity of 185 mAh g−1. Furthermore, the flexible electrode displayed exceptional both electrochemical and mechanical properties when it was bent at 180°.

![Figure 2. Synthetic processes of the MCNTs-PANI-[PMo12O40]3- nanocomposite.](image)

3.2. Silicon-polyaniline composite anodes
Wu et al. [6] reported the conductive PANI as a binder and conductive agent to cover Si nanoparticles (NPs) in a 3D porous framework via the in situ polymerization process (Figure 7). As anode material for Li-ion battery, this ternary nanostructure presented a stable discharge capacity of 1200 mAh g−1 after 1000 cycles (Figure 3). The 3D porous PANI matrix can not only improve the electrical conductivity of the total nanocomposite, but also prevent the Si NPs from decomposition in electrolyte through the stable SEI layer. In addition, the PANI coating strategy is able to supply enough free space for volume change during the charge-discharge process, resulting in excellent cycling stability of the Si material. According to the study of Wu et al., the formation of bifunctional PANI binders are always influenced by the dopants. The formed hydrogen bonds between phosphoric acid and SiO2 can promote the reaction of phytic acid molecules with the Si surface. The nitrogen-containing groups on the PANI can be protonated by the superfluous phosphoric acid on the surface of Si, thus contributing to strong interactions with Si and forming the three-dimensional cross-linked conductive networks. Lin et al. [7] reported the 5-sulfoisophthalic acid (SPA) doped PANI. In this structure, the SPA is able to enhance the connections between the PANI and Si NPs, meanwhile, the SPA-doped PANI covers the Si NPs to further stabilize the structure of the active Si material and improve the total electrical conductivity. As anode materials, the obtaining SiNP@PANI/SPA nanocomposite demonstrate a high specific capacity up to 950 mAh g−1 after 1000 cycles.
3.3. Metal oxides-polyaniline composite anodes

As the core materials, the metal oxides are always protected by PANI shell from dissolution in acidic electrolyte. And conductive PANI can also enhance the electrical conductivity of the metal oxides. Xia et al. [8] synthesized core-shell Co$_3$O$_4$/PANI nanoarrays with adjustable PANI shell morphologies under different electrodeposition. PANI nucleated on the surface of Co$_3$O$_4$ to protect core material from structure destruction and acid dissolution, resulting in the prolonged cycle life accompanied with a high capacity up to 695 mAh g$^{-1}$ at 1.5 A g$^{-1}$. The template-processed sandwich-like PANI/SnO$_2$/PANI composite nanostructure was prepared by Ding et al. [9] The MnO$_2$ template was firstly covered by the protective PANI layer, which can effectively promote the redox reaction between Sn$^{2+}$ and MnO$_2$, thus leading to the formation of the PANI/SnO$_2$/PANI nanocomposite (Figure 4). The protective PANI layer into active SnO$_2$ material can increase electronic conductivity and improve Li$^+$ storage capability. Moreover, the PANI interlayer is able to buffer the volume changes originated from the charging/discharging cycling. Electrochemical tests suggest that PANI/SnO$_2$/PANI nanocomposite demonstrated a high specific capacity up to 568 mAh g$^{-1}$ at 1A g$^{-1}$ after 100 cycles. Recently, Venkata et al. [10] fabricated the SnO$_2$/PANI nanocomposite by a solution-route process and a calcination strategy. Thermal stability measurements indicated that the PANI protected SnO$_2$ nanostructure show better stability than pure SnO$_2$ nanoparticles. Using as anode material for Li-ion cell, the SnO$_2$/PANI nanocomposite presented an ultrahigh reversible capacity of 1450 mAh g$^{-1}$ at 0.1C.
Figure 4. Preparation and cycling performance of sandwich-like PANI/SnO$_2$/PANI hybrid electrode.

4. Conclusion

Conducting polyaniline is of great research interest to use as anode material for Li-ion batteries. Recent progresses and efforts about the PANI based materials were discussed and reviewed in this paper. Conducting PANI can increase electronic conductivity and improve Li$^+$ storage capability. It is also able to buffer the volume changes originated from the charging/discharging cycling. All these properties indicate that PANI have great potential in the application of energy storage. However, there are still some issues for PANI need to be further concerned. For instance, both temperature and pH value can greatly influence the electrical conductivity of PANI and dopants. To sum up, the research and application of PANI is still in the developing stage, it can be predicted that its application will be more and brighter in the future.

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