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The Effect of Doping Type on the Performance of Secondary Batteries Based on PANI/Zn

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Abstract. Polyaniline (PANI) was successfully synthesized by the rapid mixing polymerization method at room temperature. Effect of doping with 1 M HCl, 1 M H_2SO_4, and 3 M H_3PO_4 in PANI synthesis process on chemical characteristics was investigated with FT-IR and UV-Vis spectrophotometers, while battery performance was tested physically with a set of multimeters. This study also investigated the chemical characteristics of different PANI doping at different levels of oxidation using Emeraldine Salt (ES), Emeraldine Base (EB), and Pernigraniline Base (PEG). The FT-IR result of PANI-ES characteristic of each doped showed typical PANI absorption at wavenumbers of 3437, 3166, 1611, and 1307 cm^{-1}, indicating the absorption of -N-H, -C-H, -C=C, and -C-N. At PANI-EB level oxidation, PANI absorption appears at wavenumbers of 1497, 1299, 1140, and 812 cm^{-1}, which indicated the absorption of -C-N, -C-N, -C=N, and -C-H, while the quinonoid (Q) and benzenoid ring (B) of PANI-EB appeared at 1590 and 1497 cm^{-1}. At PANI-PEG level oxidation, PANI absorption appears at 1304, 1150, and 830 cm^{-1}, indicating the absorption of -C-N, -C=N, and -C-H, while the Q and B ring of PANI-PEG appeared at 1589 and 1501 cm^{-1}. Characteristic of PANI with UV-Vis showed the maximum absorbance of PANI at 365-408 nm and 575-626 nm, which indicated the transition of $\pi \rightarrow \pi^*$ in Q and B rings. Performance testing of PANI/Zn battery for each doping was tested 6 times for 60 minutes. The highest PANI cell potential value obtained by PANI-PEG/Zn with H_2SO_4 doping was 1.01 Volt, and the lowest PANI cell potential resulted from PANI-EB/Zn with the doping of H_2SO_4 was 0.1 Volt.

INTRODUCTION

Batteries are one of the electrical energy storage media that are commonly used today, ranging from clocks, portable devices to electric cars. There are 2 types of batteries, namely primary batteries and secondary batteries. Secondary batteries are more commonly used. One type of secondary battery that is widely used today is the Lithium-ion (Li-ion battery). However, developing secondary batteries still have drawbacks. The secondary lithium-ion battery has a short lifetime period, quickly degrades when exposed to heat due to its high sensitivity, will be destroyed if it is completely depleted, expensive to manufacture, and not safe to the environment [1]. Secondary lithium-polymer usually have short use cycle, only about 300-400 cycles, also very sensitive that it can cause fires, and requires special maintenance. The Nickel-Metal Hydride (Ni-MH) secondary battery is expensive and cannot absorb overcharge well [2]. Currently, many chemical compounds-based batteries have been developed, in which are more potential to be used as an alternative to the Li-ion battery. One of that is Polyaniline (PANI). PANI is a conductive polymer that has several advantages over other conductive polymers, such as excellent chemical and physical stability, reversible redox response, wide conductivity range, and can be synthesized by several methods [3].

PANI as one type of conductive polymer active materials can be used as energy storage media and conversion devices other than carbon materials and metal compounds. PANI has high specific capacitance, high flexibility, low cost, and also has great potential in its application as a super capacitor [4]. Supercapacitor electrodes with high energy storage capability and long-life cycles have begun to be developed such as in PANI composites with carbon or inorganic pseudo capacitors [5]. PANI is a type of conductive polymer formed from aniline monomer ($C_6H_5NH_2$) [6],

has properties that are easy to synthesize, high stability to the environment, easy to change its conductivity by doping, and is corrosion resistant [7]. There are several methods that can be used to synthesize PANI, such as the one-pot method for the synthesis of polyaniline wrapped in air gel/silver graphene [8], Galvano dynamics [9], Green synthesis [10], chemical oxidation [11], interfacial and hydrochloric acid dopants addition [12], electrochemical [13] and rapid mixing polymerization [14]. Each method has advantages and disadvantages, and the method used to synthesize PANI is the method that is often used by researchers, the electrochemical method, and chemical oxidation.

Rahayu, *et al*. (2015) [12] succeeded in synthesizing PANI with the interfacial method and the addition of hydrochloric acid as doping and applied it as a material for making batteries. The addition of doping succeeded in increasing the conductivity from PANI of 0.03 to 0.07 S.cm^{-1}, with PANI in the undoped state having a low conductivity of 10-10 S.cm^{-1}. However, the research of Rahayu, *et al*. (2015) [12] is only limited to the use of commonly used acid doping, the energy capacity produced is also still low, but on the other hand, it turns out that the effect of doping on synthesis of PANI greatly affects to the energy storage produced. Therefore, further research is needed on variations in the types of doping. This research has been conducted in several steps, which includes the synthesis of PANI on different doping types, characterization of PANI powder, electrolyte manufacture, and performance testing. The method that will be used to synthesize PANI is rapid mixing polymerization with the addition of different doping referring to the research of Richard and Didik (2014) [15] who succeeded in producing a PANI electrical conductivity of 35.38 S.cm^{-1} compared to PANİ in the undoped state. This research was carried out by various types of doping. In this research, doping type is from 1 M HCl, 1 M H$_2$SO$_4$, and 3 M H$_3$PO$_4$, then the characterization of PANÍ has been carried out using a UV-Vis spectrophotometer and FT-IR, then the electrolyte made from a solution of 1M Potassium Chloride (KCl). The final stage is to test the performance of the battery by looking at the potential difference generated.

EXPERIMENTAL METHOD

Materials

Polyaniline (PANI) was prepared by the method of rapid mixing polymerization of the aniline monomer (C$_6$H$_5$NH$_2$) (ρ=1.02 g/cm^3) with various types of doping. The type of doping to be used are 1M hydrochloric acid (HCl), 1 M sulfuric acid (H$_2$SO$_4$), and 3 M phosphoric acid (H$_3$PO$_4$). The product was characterized using FT-IR spectrophotometer and UV-Vis using a solvent of N-Methyl Pyrrolidone (NMP). The results were in a prototype battery with an electrolyte solution of 1 M Potassium Chloride (KCl) and the potential difference generated by a series of physics experiments, then will result from the performance of the prototype batteries of PANI/Zn.

Synthesis of PANI

One gram of aniline monomer was dissolved in 3 different types of doping, 1 M HCl, 1 M H$_2$SO$_4$, and 3 M H$_3$PO$_4$. The synthesis of PANI was carried out by the rapid mixing polymerization method [14] from solutions A (aniline + doping) and B (oxidizing agent in aqueous media) which were mixed simultaneously at room temperature along with mixing or stirring with Ammonium Persulphate (APS) as the oxidizing agent. The polymerization process will continue after mixing the two solutions until a precipitate is formed and a color change occurs. At the end of the polymerization, a dark green color will be formed which indicates the PANI polymerization process has been completed.

Characterization

The synthesized PANI powder was characterized by two spectrophotometer instruments, Fourier Transform Infrared (FTIR) and Ultra Violet-Visible (UV-Vis). FT-IR spectrum of PANI powder samples was recorded in the wavenumber of 400-3500 cm^{-1} with PerkinElmer Frontier and Spectrum Two, while UV-Vis spectrum of PANI samples was recorded in the wavelength of 400-900 nm with spectrophotometer UV-Vis by Shimazu UV-1601PC.

RESULTS AND DISCUSSION

Polyaniline has great potential to be developed as a secondary battery. This is because polyaniline has three relatively stable oxidation states (Figure 1.). Emeraldine base (EB) is the most stable polyaniline oxidation level, where in theory it is known that at the EB level, there is one quinonoid ring unit in every 4 repeat units. Meanwhile, Leucoemeraldine Base (LEB) is a lower oxidation level than EB, where each repeating unit is a benzenoid ring. Pernigraniline base is the highest oxidation level of polyaniline, where in every 4 repeat units there are two alternating quinonoid rings and two benzenoid rings.
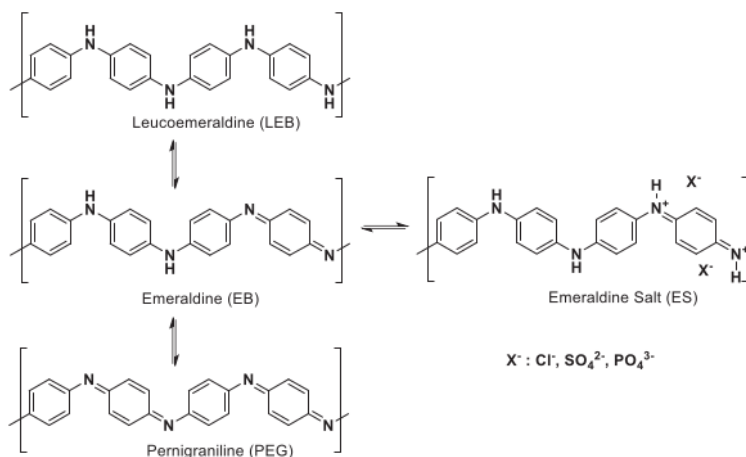

FIGURE 1. Polyaniline in various oxidation level and protonated process by acid

Synthesis of PANI on Various Types of Doping

The synthesis of PANI was carried out by the rapid mixing polymerization method of solutions A (aniline + dopant) and B (oxidizing APS in aqueous media), which were mixed simultaneously at 273 K along with the mixing or stirring process. This method was chosen because PANI can be produced on a large scale, and the separation process is easy. In this process, the polymerization of aniline is exothermic, and the rapid mixing reaction causes an increase in the temperature of the mixed solution.

TABLE 1. Polymerization time reaction of PANI on different doping types (in second)

Aniline + doping	Polymerization time (second)					
Aniline + HCl 1M	25	30	40	45	50	58
Aniline + H_2SO_4 1M	20	30	45	50	48	65
Aniline + H_3PO_4 3M	20	30	35	40	45	53
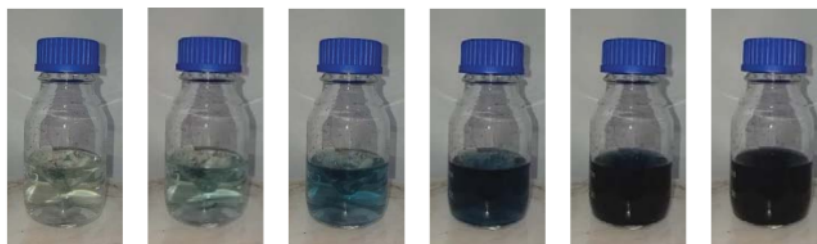
When the polymerization reaction and formation of PANI precipitates occurs, the initiator molecule will be depleted during the formation of PANI. This is what happens in the polymerization reaction with HCl doping at 45 to 58 seconds of mixing. In the polymerization reaction of all types of dopants there was a significant color change from colorless to sky blue, dark blue and finally to dark green which indicated that the polymerization reaction had ended. Table 1 shows that the doping concentration used affects the polymerization reaction time. This is in line with the research of Zakaria *et al.*, (2015) [14] who found that the time of color change and polymerization reaction depended on the concentration of HCl or doping, and optimum conditions occurred at high doping concentrations. This is why the polymerization reaction of PANI doped with 3 M H_3PO_4 is faster than another dopant.

Characterization of PANI

FT-IR Characterization

Characterization of doped PANI was carried out using the Perkin Elmer Frontier FT-IR Spectrum at the Analytical Chemistry Laboratory of University of Mataram by pounding PANI powder with KBr, then making it into pellets and measuring its absorption at a wavenumber of 3500-500 cm^{-1}.
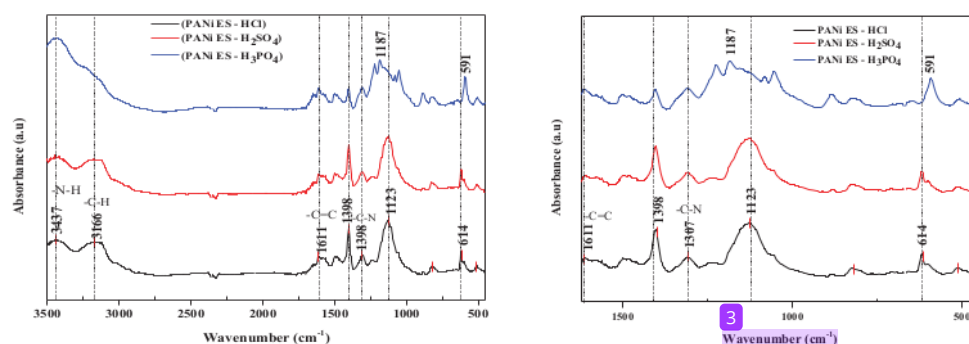

FIGURE 2. FT-IR Spectrum of Emeraldine Salt in various acid dopant (left) and magnification of fingerprint region (right)

Absorption at 3437 cm^{-1} wavenumber is indicated as strain vibration of–N-H according to research by Zareh [16] and Prasutiyo [17] who synthesized PANI-ESor PANI-LEB in the same way and obtained absorption at 3421 and 3426 cm^{-1}, respectively. The same thing happened to the absorption at 1307 cm^{-1} which was indicated as –C-N vibration according to the results of the synthesis from Zareh [16], Wibawanto [18] and Prasutyo [17] who obtained –C-N vibration at 1298, 1273 and 1299 cm^{-1}. The synthesized -C=C vibration was obtained at 1611 cm^{-1}, in accordance with the research of Wibawanto [18] with a -C=C vibration at 1569 cm^{-1}. Then the –C-H stretching vibrations of PANI-ES all doping were obtained at a wavenumber of 3166 cm^{-1} (Figure 2).
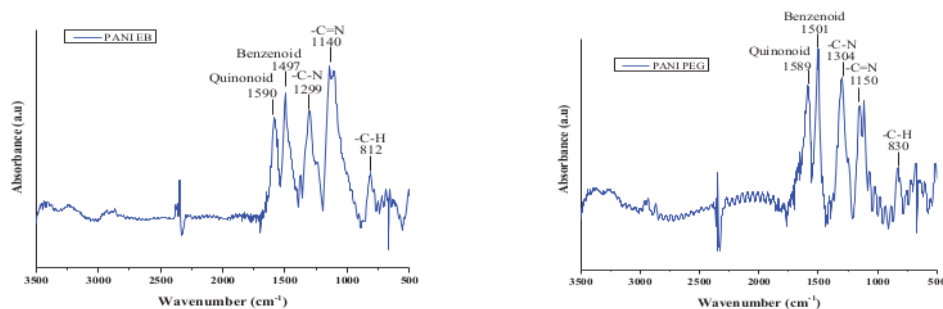

FIGURE 3. FT-IR spectrum of Emeraldine base (left) and Pernigraniline base (right)

In the spectrum of FTIR PANI-EB, wavenumbers of 3000 cm^{-1} and above do not show clear absorption, unlike in PANI-ES. This is because, in the PANI state of the EB oxidation state, the hydrogen bonds between the chains with each other in –N-H are very strong. However, when the doping process takes place, the imine group on the quinonoid will be protonated or bind to H$^+$. This condition is called bipolaronic which will continue to resonate. This is what causes the absorption in the region of 3000 cm^{-1} and above in PANI-ES with PANI-EB contrasts. The bipolaronic condition in PANI-EB is also influenced by the protonation agent or dopant used. The stronger the dopant acid used, the faster the bipolaronic and resonance conditions take place. In the PANI-PEG FT-IR spectrum, the resulting spectrum is almost similar to the PANI-EB spectrum. Figure 3. is the FT-IR absorption spectrum of PANI-PEG in the wavenumber range of 500-3500 cm^{-1}. The main peaks at 1501 and 1589 cm^{-1} are the peaks of the presence of benzenoid and quinonoid rings. Another vibration that appears is stretching –C-N at 1304 cm^{-1}, while the –C=N appears at 1150 cm^{-1} from the quinonoid ring, and bending vibration –C-H appears at 830 cm^{-1}.
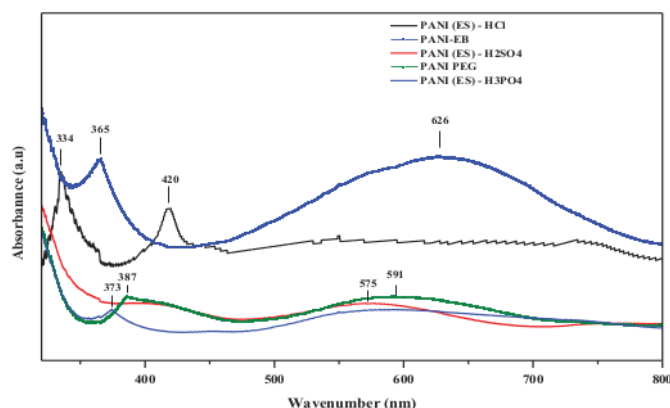
Characterization with UV-Vis Spectrophotometer

FIGURE 4. UV-Vis Absorption of polyaniline in various oxidation state and acid doped

The wavelength graph of the absorbance of PANI-ES powder in this study shows that there are 2 maximum absorption peaks at 365-408 nm wavelength, which are electron transitions $\pi \rightarrow \pi^*$ on the benzenoid ring along the PANI polymer chain. Another absorption peak is at 575-626 nm (Figure 4.), which is the transition of electrons $\pi \rightarrow \pi^*$ on the benzenoid ring to the quinonoid ring where the possibility of this transition is only between chains.

Electrolyte Solution

Battery conductivity is also affected by the presence of an electrolyte solution used. According to Khan *et al.*,[19] conductivity follows the order of the atomic radius of the alkali metal or K$^+$> Na$^+$. In general, polymeric substances retain a small number of water molecules; and in that way when the PANI material is in contact with the electrolyte solution, the movement of each species into the polymer is entirely dependent on the segmental mobility of the polymer. In addition to the segmental mobility of the polymer, the diffusion capacity is also affected by the possibility that the segment can form a hole large enough to accommodate the species that diffuses around it. Universally, the conductivity of any material in an electrolyte solution depends entirely on the number of ions that the electrolyte solution can produce. Under the same conditions, a solution with a higher number of ions has a higher conducting energy than another solution with the same concentration but a smaller number of ions. Further observation of the conductivity of the KCl solution showed that the degree of dissociation of KCl> NaCl. This is what underlies the use of KCl electrolyte solution in this study.

Performance Testing

The performance test of the secondary battery is carried out by physical instruments with a multimeter on the potential difference (Volts) of the designed battery. The prototype PANI/Zn secondary battery consists of ITO glass, PANI sticking on ITO, separator membrane, and Zn metal plate.

TABLE 2. Perfomance testing of PANI

Anode/Cathode	E_{Cell} (Volt)	E^o (Zn/Zn^{2+}) (Volt)	E_{anoda} (Volt)
ES(HCl)/Zn	0.30	-0.25	0.05
ES(H_2SO_4)/Zn	0.40	-0.25	0.15
ES(H_3PO_4)/Zn	0.30	-0.25	0.05
EB/Zn	0.90	-0.25	0.65
PEG/Zn	1.10	-0.25	0.85

$$ES(HCl) + 2e + Zn \rightleftharpoons LEB_{(s)} + Zn^{2+}_{(aq)} \tag{1}$$

$$ES(H_2SO_4) + 2e + Zn \rightleftharpoons LEB_{(s)} + Zn^{2+}_{(aq)} \tag{2}$$

$$ES(H_3PO_4) + 2e + Zn \rightleftharpoons LEB_{(s)} + Zn^{2+}_{(aq)} \tag{3}$$

$$EB + 2e + Zn \rightleftharpoons LEB_{(s)} + Zn^{2+}_{(aq)} \tag{4}$$

$$PEG + 2e + Zn \rightleftharpoons EB_{(s)} + Zn^{2+}_{(aq)} \tag{5}$$

Each PANI oxidation level has different conductivity values. An emeraldine base is a PANI oxidation level that has a higher conductivity value compared to other PANI oxidation levels and other polymers but lower compared to metals [20] Doping of 3 M H_3PO_4 shows an average lower potential difference value, which is caused by the degradation of polymer chain structure due to high acid concentrations [14]. The high performance of the potential difference generated by PANI/Zn will be obtained in the PANI state with a high reduced range, or from PANI PEG to PANI ES or LEB, while the chemical structure of PANI with high performance will be obtained at the oxidation level with a stable PANI structure, at the PANI EB level.

CONCLUSION

Polyaniline (PANI) was synthesized by rapid mixing polymerization method on various doping types and PANI oxidation levels. The doping types used were 1 M HCl, 1 M H_2SO_4, and 3 M H_3PO_4. The highest performance of the PANI/Zn secondary battery was produced from PANI(PEG)-H_2SO_4/Zn of 1.01 V as much as 0.0655 g PANI on ITO glass, while the lowest performance of the PANI/Zn secondary battery was produced from PANI(EB)- H_2SO_4/Zn of 0.1 V as much as 0.0699 PANI on ITO glass. This means the doping type on PANI synthesis also give different results of performance and properties of PANI.

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FINAL GRADE

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GENERAL COMMENTS

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