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Influence of Electrolyte Concentration on Statics and Dynamic Lead-Acid Battery

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Abstract. Electrolyte concentration is one of the important parameters on Lead-Acid Battery (LAB) outcome. Lead-acid battery has been made with static and dynamic electrolyte treatment where 4 variations of electrolyte concentration (20%, 30%, 40% and 50%) and 1A current applied in the system during charging-discharging test to analyze the relationship of the electrolyte concentration to the battery characteristic and compare static and dynamic lead-acid battery performance. The experiment result that for dynamic lead acid battery, the capacity increases along with the higher concentration from 20% to 40% but decrease at 50% compare to 40% for 3 first cycle charge-discharge test when the static lead-acid battery unwork at concentration 20% and show the increases capacity along with increases concentration. In capacity and efficiency point of view, dynamic lead-acid show better performance compare to static lead-acid battery.

Keywords: Lead-Acid, Renewable Energy, Electrolyte Concentration, Capacity, Battery

INTRODUCTION

The using of renewable energy as an electricity source is one of the solution for a high electricity demand in a condition where the fossil fuels availability is continue to decrease. The main obstacle of the renewable energy power plants is the uncertain weather. An energy storage system is needed in the electric grid of renewable energy [1-3]. A large capacity, long life-cycle and cost-effective are factors to consider in energy storage system [4]. Batteries are components that can store and produce electrical energy by converting chemical reactions (reduction-oxidation). Batteries consist of a pair of electrodes and electrolytes [1]. Basically, batteries are divided into non-rechargeable (primary) batteries and rechargeable (secondary) batteries where [2].

A dynamic battery (redox flow battery) is a secondary battery in which the active materials of the battery are in separate containers. Dynamic batteries have the advantage of increasing battery capacity or performance by modifying only a component (cell or chamber) [3]. Dynamic batteries are being developed as large-scale energy storage units in renewable power plants due to its high capacity, high efficiency and long life-cycle [5,6] [4,5]. Electrolytes of the dynamic batteries are in a chamber while the electrodes in a battery cell. Electrolytes are pumped through the cell, causing a redox reaction in the battery cell [5]. Dynamic batteries are divided into double-electrolyte and single-electrolyte. The double-electrolyte dynamite batteries use two different types of electrolyte, so

that an ion-separation membrane components are required. The single-electrolyte dynamic batteries use only one type of electrolyte [6]. The single-electrolyte dynamic battery has several advantages due to no ion-separation membrane is needed, so the manufacturing becomes easier and the costs required is lower, and some problem with the double-electrolyte dynamic battery membrane can be ignored since there is no ion exchange through the membrane and the chemical reaction takes place directly [7].

Lead-acid battery is a type of battery that has been developed as a dynamic battery. Zang (2011) provides the performance of lead-acid dynamic battery which have a performance as good as conventional batteries [8]. In 2017, Ghufron and Kurriawan have compared lead-acid dynamic batteries with conventional battery (accumulator). The lead-acid dynamic battery has a better performance than the accumulator, as indicated by a dynamic battery energy efficiency of 67.9%, while batteries have an energy efficiency of 35.5% [9].

Electrolytes are one of the parameters that affect a battery performance. In 2015, to Akbar and Lapanoro compared the performance of Cu-Zn battery with different electrolyte types and concentrations. Different electrolyte concentrations produce different battery powers. In the Cu-Zn battery with H_2SO_4 as electrolyte, the battery voltage is maximum at H_2SO_4 29.134%, which is equivalent to the standard concentration of H_2SO_4 used in the accumulator, which is between 29% and 32% [13].

In this study, lead-acid dynamic batteries with 4 variations of H_2SO_4 concentration with a certain range between and above the standard H_2SO_4 concentration in lead-acid conventional battery are tested for the charge-discharge cycle to determine the battery characteristic. The comparison between the lead-acid dynamic and conventional battery is presented. Both batteries are 3 series cells batteries with the same electrolyte of H_2SO_4 .

METHODS

In this study, the lead-acid battery used is a single cell battery, which consist of only one pair of negative and positive electrodes in a battery cell. The main components of the lead-acid flow battery are a battery cell, an electrolyte chamber, a micro-pump and battery active materials. The battery active materials are electrodes and electrolyte. The electrodes used in the battery system are lead (Pb) and lead dioxide (PbO_2) plates with size of 13.5 cm x 7.5 cm. The electrolyte is sulfuric acid with 4 different concentrations (20%, 30%, 40% and 50%). The Pb and PbO_2 plates were arranged with 3 mm gap between them inside the battery cell with. A separator membrane were placed between the electrodes to prevent a short circuit.

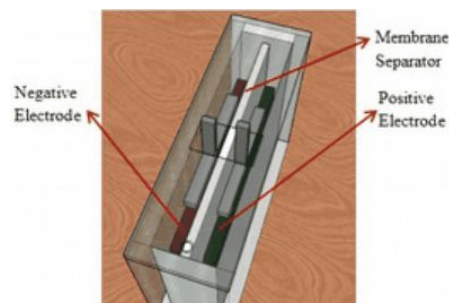


FIGURE 1. The arrangement of electrodes in the battery cell

The battery cell and chamber were connected by a transparent rubber tube. The electrolyte were then pumped through the rubber tube, from the chamber into the battery cell using micropump. The electrodes inside the battery cell were completely drowned by the electrolyte. The total volume of electrolyte used for a single cell battery is 400 ml with a flow rate at 9 ml/minute.

The testing of the battery characteristics (charge-discharge) is done by the BMS (Battery Management System) namely *Turnigy Accucell-6 50 w*. The current, voltage and capacity data from the battery tests were recorded using *ChargeMaster2.02*, a software that has been integrated into the *Turnigy Accucell-6*. The battery charge-discharge tests were performed in 3 cycles with charge and load currents at 1 A for each lead-acid battery

with varying H_2SO_4 concentrations. In this tests, a constant current method are apply for the charge-discharge tests, with a maximum charge voltage is 2.41 V and minimum discharge voltage is 1.81 V.

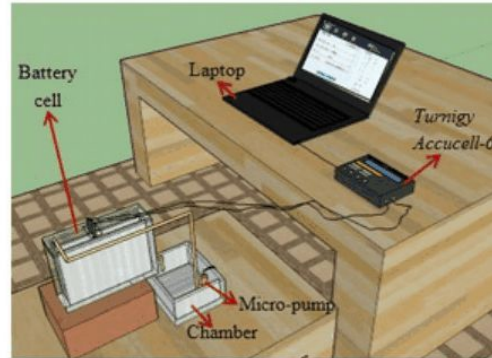


FIGURE 2. The arrangement of the lead-acid battery and the battery testing tools (*Turnigy Accucell-6*, laptop and *ChargeMaster2.02*)

A static lead-acid battery were used as a comparison to the dynamic battery. The static battery has a similar arrangement as the dynamic battery. The electrolyte of the static battery wasn't flowed through chamber and battery cell, so the rubber tube connection was terminated and there was no circulation of electrolyte in the battery cell as the dynamic battery. A variation of electrolyte concentration were also applied in the static battery. A different pair of electrodes were used for each variation of system, and a pre-tests discharge (each system were discharge until its voltage dropped at 1.81 V) were done so that each system has the same starting point for the charge-discharge tests.

RESULTS AND DISCUSSIONS

Charge-Discharge Characteristics

The spontaneous reaction between $Pb-PbO_2$ and H_2SO_4 in lead-acid batteries occurs during the discharging process. The reverse of the spontaneous reaction can occur by supplying energy to the battery, which we called by a charging process. During charging, the battery voltage increases, indicating an electrical energy storing in the battery. Based on Fig. 3, the battery voltage during charging is increasing from the value of the battery open voltage to the initial charging voltage that occurs due to an internal resistance of the battery. The battery voltage rises to 2.41 V and then remains constant at 2.41 V until battery charging is completed.

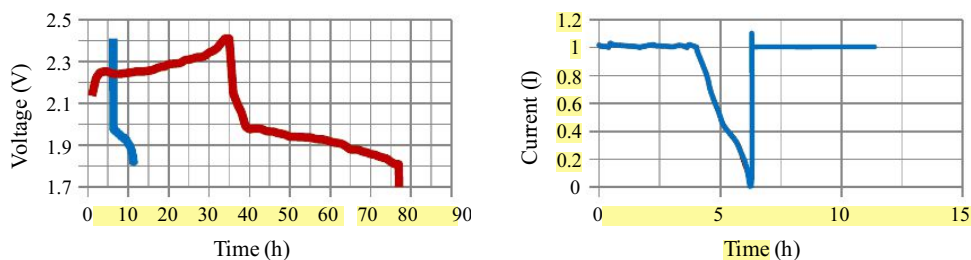


FIGURE 3. Voltage to time (V-T) graph and current to time (C-T) graph of 1 charge-discharge cycle of lead-acid dynamic battery with H_2SO_4 40%, red line for charging and blue line for discharging

H_2SO_4
40%

At the constant battery voltage of 2.41 V, the originally constant charging current 1 A has dropped to a minimum current of 0.09 A, which indicates that the charging process has reached its final stage. The battery charging process stops or ends when the minimum current is reached, ie no charge can be stored by the battery. During discharging, the battery voltage decreases from the value of an open voltage to the initial discharge voltage due to the battery internal resistance. The battery voltage then decreases slowly, which indicates that the battery were releasing its stored energy. The battery discharge current is set to be constant at 1 A. The battery discharge stops when the battery cut-off voltage of 1.81 V is attained. Both dynamic and static batteries have similar characteristic.

Voltage of Dynamic battery characteristic based on the variation of H_2SO_4 concentration and the comparison to the static battery

Figure 4 is a V-T graph for 3 charge-discharge cycles of the lead-acid dynamic battery, it shows that a battery with higher H_2SO_4 concentration has a longer time for each cycle. This indicates that there is more reaction occurs in the battery with high concentration. In addition, the initial charge and discharge voltage is higher for batteries with higher H_2SO_4 concentrations. This shows that the battery voltage changes in a more positive direction as the H_2SO_4 concentration increases, which can be explained by the Nernst equation [12, 14]. The dynamic battery with H_2SO_4 50% (50% dynamic battery) has an initial charge voltage that is relatively higher than other dynamic batteries. This leads to the fact that at H_2SO_4 50%, the maximum charge voltage were attained faster and the decreasing of charge current occurred in a longer time. As a result, the 50% dynamic battery charge capacity in cycles 1 and 2 were less than the 40% dynamic battery charge capacity, although the dynamic charging process takes longer time. Based on Fig. 4, it is known that all the examined lead-acid dynamic battery are rechargeable.

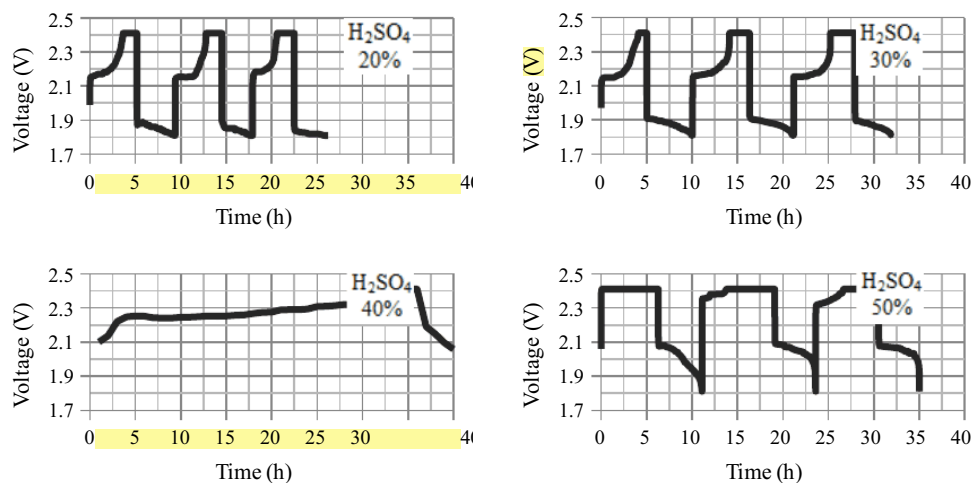


FIGURE 4. Voltage to time (V-T) graph of lead-acid dynamic batteries with 4 variations of H_2SO_4 concentration for 3 charge-discharge cycles

The dynamic battery discharge voltage increases with the increasing of H_2SO_4 concentration. This shows that there is more energy released in the battery with higher H_2SO_4 concentration. From Fig. 4 we could also see that the discharging process of the battery with higher H_2SO_4 concentration stops at voltage above the cut-off voltage at 1.81 V. The discharge voltage of the battery with higher H_2SO_4 concentration dropped suddenly, this shows that the discharging process is limited by the electrode surface area, the chemical reaction stopped since the electrode surface is already covered up by the $PbSO_4$ crystal which is an insulator.

Figure 5 below presents the V-T graph of the static dynamic batteries for 3 charge-discharge cycles. H_2SO_4 concentration that is lower than 30% is not compatible for the static battery, because the static battery does not have a more electrolyte supply like the dynamic battery so the ions supply is not enough for the battery to produce electricity with the same criterion (1 A current supply). If we compare the dynamic and static battery, we could see that most of the dynamic battery has longer charge-discharge cycle than the static battery. This shows that there is more chemical reaction in the dynamic battery than in the static battery, which is caused by the amount of ions in the electrolyte and the electrolyte condition (flow and static). There is possibility to strip the PbSO_4 deposits and decrease the crystals that accumulate on the electrode due to the flowing electrolyte. As the PbSO_4 on the electrode decrease, the reaction that occurs between the electrolyte and the electrode does not have a major barrier that interferes with the **reaction**.

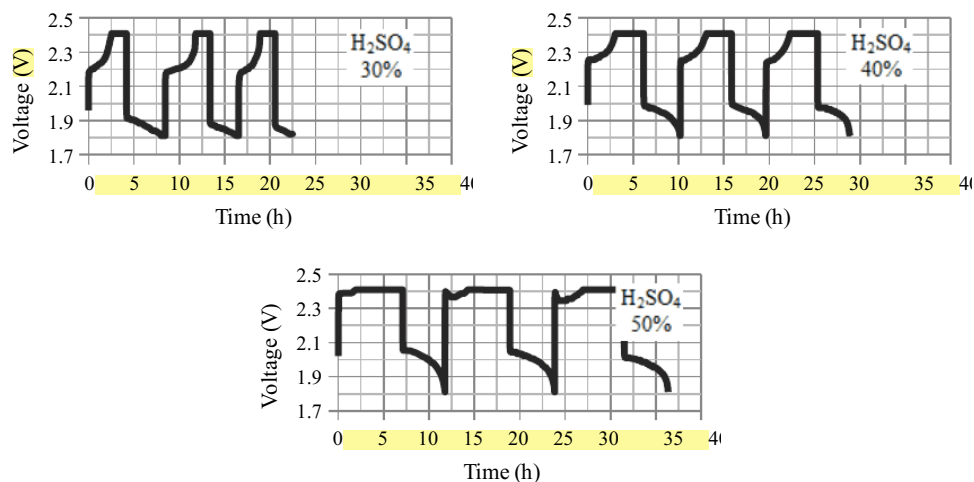


FIGURE 5. Voltage to time (V-t) graph of lead-acid static batteries with 3 variations of H_2SO_4 concentration for 3 charge-discharge cycles

Comparison of Capacity

The capacity or energy storing of the battery is given in ampere-hours (Ah) at certain voltage and current values [15]. The battery capacity indicates the amount of electrical charge that can be released by the battery. Figure 4 shows that the battery with higher H_2SO_4 concentration has a longer the battery discharge time. The battery discharge time is proportional to the battery capacity with a constant discharge current at 1 A. From Fig. 5 below, it is known that at the concentration range of 20 to 40%, the average battery capacity increases with the increasing of H_2SO_4 concentration. Meanwhile, the average capacity of the 50% dynamic battery is lower than the average capacity of the 30% and 40% dynamic battery.

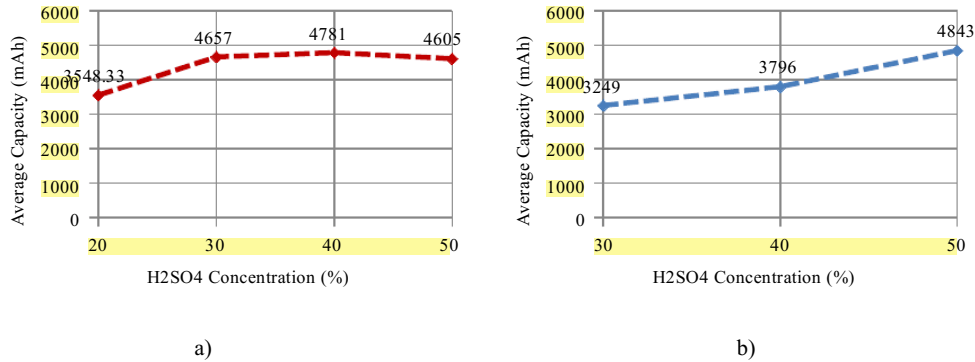


FIGURE 5. Average capacity to H₂SO₄ concentration graph for: a) dynamic battery and b) static battery

The average capacity of the 20% dynamic battery differs significantly from the average capacity of the 30%, 40% and 50% dynamic batteries. Meanwhile, the average capacity between the 30%, 40% and 50% dynamic batteries has a relatively small difference. This shows that the battery capacity at concentration of 30% and more is limited by the area of the electrode, and at concentration of 20% (which has the same electrode area) is limited by H₂SO₄ concentration. This corresponds to the experiments of Pavlov (2006), a 12 cell batteries can be divided into two types, the P-type with H₂SO₄ concentrations >1.24 g/cm³ and the H-type with H₂SO₄ concentration ≤1.24 g/cm³. The battery capacity of the P-type is limited by the electrode plate and the H-type is limited by H₂SO₄ concentration [14]. Based on Figure 5, we could see that the dynamic battery capacity is higher than the static battery capacity at the same H₂SO₄ concentration. This shows that the addition of electrolyte in the chamber on the dynamic battery increases the battery capacity. The 50% dynamic battery capacity is lower than the 50% static battery capacity. Meanwhile, the 40% dynamic battery capacity is almost the same as the 50% static battery. This shows that the dynamic battery discharge performance is not maximum at such high H₂SO₄ concentration.

2.1 Efficiency

The efficiency is a comparison between the energy delivered by the battery to the energy required by the battery during the charging process. The amount of energy generated by with certain voltage (V) and current (I) for a given period of time is:

$$E = VI \Delta t \quad (1)$$

Thus, battery energy efficiency is [8]:

$$\eta_{energy} = \frac{E_{delivered}}{E_{stored}} \quad (2)$$

If the amount of the energy delivered is D (discharge) and the energy stored is C (charge), the energy efficiency can be described as follows:

$$\eta_{energy} = \frac{V_D I_D \Delta t_D}{V_C I_C \Delta t_C} \quad (3)$$

The average energy efficiency of the dynamic and static lead-acid battery is shown in Fig. 5:

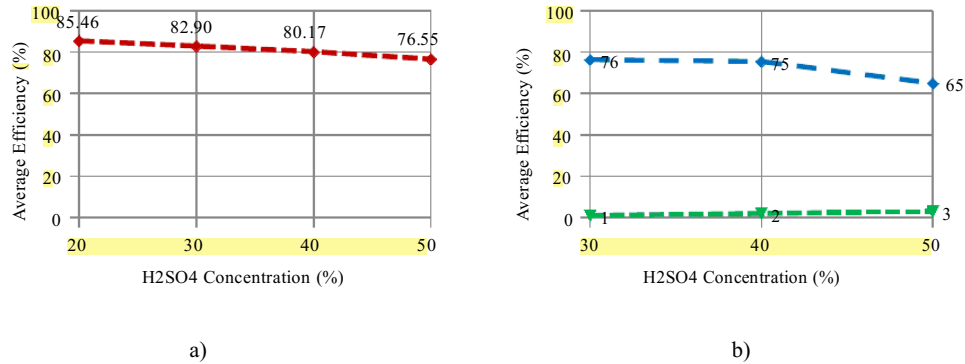


FIGURE 6. Average energy efficiency to H₂SO₄ concentration graph for: a) dynamic battery and b) static battery

Based on Fig. 6, the average energy efficiency of the lead-acid batteries decrease with the decreasing of H₂SO₄ concentration. A low energy efficiency indicates higher energy losses. The dynamic battery has higher energy efficiency than the static battery with the same H₂SO₄ concentration. This means that the ratio of the discharge energy to the charge energy is higher due to the flowing electrolyte so that the reaction is maximum in the dynamic battery. The 40% dynamic battery has a lower average energy efficiency than the 20% and 30% dynamic batteries. However, the 40% dynamic battery has the least change per cycle (Fig. 7). This shows that a 40% dynamic battery has a more stable performance than 3 other dynamic batteries. The unstable battery efficiency can occur due to the self-recovery phenomenon which happens when a battery is being rested (is not being charged or discharged) for a while.

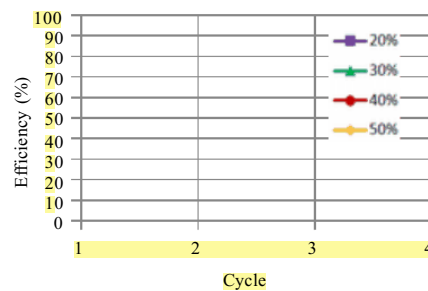


FIGURE 7. Energy efficiency graph of lead-acid dynamic batteries for 3 charge-discharge cycles

SUMMARY

The 3 cells dynamic battery has similar characteristic with the 3 cells static battery. The dynamic battery has higher capacity since it has more and flowing electrolyte which gives some advantages such as circulation of the electrolyte in the battery cell so the decreasing of electrolyte concentration is slower than the one in the static battery. The sulphation also affects the decrease of battery capacity. The lead-acid dynamic battery with Pb-PbO₂ (13.5 x 7.5) cm² as the electrode and H₂SO₄ as the electrolyte has been successfully developed, with characteristics similar to the static battery. The higher concentration of H₂SO₄ used in the battery, the higher operating voltage of the battery. The increasing of the H₂SO₄ concentration increases the battery capacity. The dynamic battery with H₂SO₄ concentrations above 30%, its capacity is limited by the size of the electrode. Meanwhile the dynamic battery with H₂SO₄ concentrations below 30%, its capacity is limited by the size of the electrode. The highest dynamic battery average capacity at 4,780 mAh is achieved at H₂SO₄ 40% with an average energy efficiency of 80.17%. The study of the dynamic lead acid battery is still ongoing, a deeper investigation is needed in order to examine the battery life

cycle more precisely such as a longer cycling test and more consideration of other parameter that affects the battery performance.

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