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Research Article

Enhancing Electrical Characteristics in a High-Power Seawater Battery: Solutions with Acid Zinc Anolyte and Alumina-Carbon-Cement Separator

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Abstract
The potential of seawater as a source of galvanic cell energy has not been fully realized due to significant challenges, particularly anode degradation in single-compartment high-power seawater batteries. This study addresses these limitations by introducing a novel two-compartment system, utilizing an acid zinc anolyte and an alumina-carbon-cement separator designed to enhance both the electrical performance and longevity of the battery. Experimental results demonstrate a remarkable increase in current output (97.81 times) and a substantial boost in power (5.25 times) compared to conventional single-compartment cells. Furthermore, the internal resistance of the system is reduced by 95.7%, indicating improved energy transfer efficiency. The use of the alumina-carbon-cement separator effectively mitigates anode corrosion, a common issue that limits the operational lifespan and reliability of seawater batteries. These findings suggest that the proposed two-compartment configuration not only overcomes critical technical barriers but also offers a promising and sustainable alternative for renewable energy generation from seawater. The enhanced performance and durability of this system highlight its potential for practical applications in marine and coastal energy harvesting, contributing to the advancement of clean energy technologies.

Keywords: acid zinc, galvanic cell, seawater, separator compositions

1. INTRODUCTION

Seawater is a highly potential natural resource as a source of electrical energy from a galvanic cell perspective [1]. This potential is related to the high electrolyte content of seawater, 3.5% in the form of NaCl and other minerals dissolved in seawater, which has a significant impact on electrochemical methods [2]. The use of galvanic cell methods is safer with high power density, long discharge voltage, and can be stored for a long time. Various battery technology developments have been carried out since the 1950s, such as Mg/AgCl batteries which have been used as a power source for electric torpedoes during World War II [3][4], and later expanded to power sound balloons, beacons, life-saving equipment, and autonomous underwater vehicles (AUV). Further developments include metal semi-fuel seawater-activated batteries (DO-type seawater batteries [5]), metal hydrogen peroxide seawater batteries [6], high power seawater battery (using high power electrodes) [7]-[9], and rechargeable seawater-activated batteries [10].

The characteristics of seawater galvanic cells are determined by the choice of negative (anode) and positive (cathode) electrodes. The use of metals in the negative sequence in the voltaic series such as lithium, sodium, magnesium, aluminum, zinc, and others can produce high power [11]. However, the reactivity and instability (explosion) of lithium and sodium must be considered from a safety perspective. Therefore, the selection of metals with safe, easily available, and cheap characteristics must be an important consideration in making seawater batteries [12]. Zinc metal is generally easy to process, does not have side reactions with seawater, is safe, and contributes to environmental fertility [13], and the dissolved zinc during discharge is easily reduced, allowing for electrode regeneration. Zinc metal has great potential to be used as a seawater electrode. Some of its drawbacks include lower voltage compared to magnesium and, in some research investigations, forming dendritic zinc crystals that can cause short circuits in batteries for battery types with very close electrode distances or without separator.

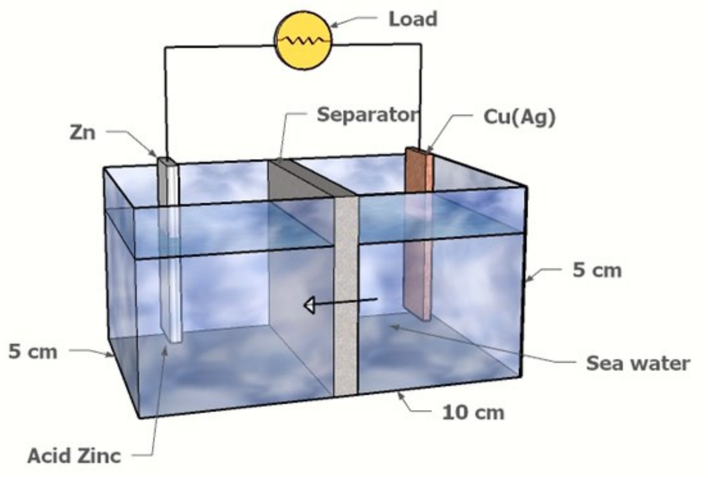

Figure 1. Two-compartment seawater galvanic cell system.

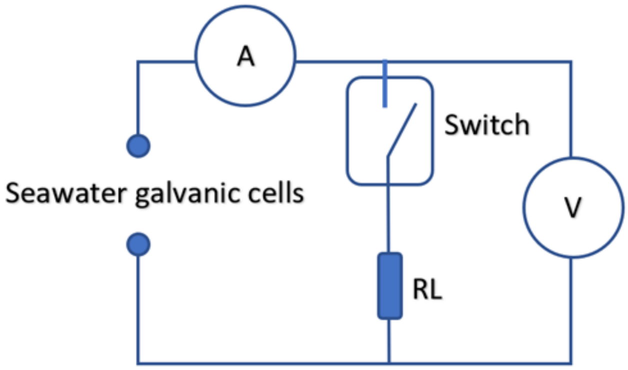

Figure 2. The electronic circuit electrical characteristics measurement [9], (switch *open* = OCV, switch *close* = CCV).

High power seawater battery uses a battery with a single electrolyte seawater compartment, and the anode and cathode electrodes use materials with a high potential difference, resulting in high voltage and current. The main problem with this method is that the anode quickly degrades and loses mass due to corrosion, making anode regeneration impossible since the oxidized electrode has reacted with various materials in seawater. This is a major obstacle in seawater batteries because the anode metal used is wasted, causing cost issues, and the anode electrode must be replaced after a certain period of time. Therefore, efforts are needed to regenerate the anode by placing it in a suitable artificial anolyte solution, which can still produce high power, or even higher, due to the better conductivity of the solution compared to seawater. In this study, the anode is placed in a low pH, acid zinc solution, and uses a separator to separate it from seawater. The use of low pH analyte and salinity in Zn will increase electron transfer between the electrolyte and the electrode [14].

Battery separators, typically composed of inorganic powders and polymer substrates, have attracted significant attention from both industry and academia [15]. Currently, most separators are made from polyolefins such as polyethylene (PE) and polypropylene (PP). These polyolefin-based separators are commercially available and exhibit superior electrochemical stability, excellent mechanical properties, and thermal shutdown capability [16]. However, they have several limitations, including excessively large pore sizes, which can result in self-discharge and internal short -circuiting. To address this issue, inorganic materials such as Al_2O_3 and SiO_2 are incorporated. These additives not only reduce pore size but also enhance thermal stability and mechanical rigidity, preventing surface cracks or bulges in the separator [17]. Recent studies have demonstrated that using Al_2O_3 and carbon as an interlayer separator improves specific capacity, cycle stability, and electronic conductivity [18]. Given these advantages, this study investigates the application of Al_2O_3, carbon, and cement, with seawater as a solvent.

Ag is one of the noble metals with higher conductivity and corrosion resistance than other metals. Ag is used on the metal surface to protect from oxidation on other metals and to add aesthetics. The price of pure Ag is quite high and considered inefficient if used directly as an electrode. Thus, a solution with Cu electroplating with Ag is a solution to improve electrode quality, which is then denoted as Cu(Ag), done as an alternative step to save costs while still producing higher electrical power. In this study, the electrode pair used is Cu(Ag)-Zn. The direct use of Cu in electrochemical cells can cause electrode passivation due to $CuCl_2$ deposits on the metal surface. To reduce passivation, one effective way is to coat the metal with another metal more resistant to corrosion [19], simple and low-cost [20]. The novelty in this study is the reported modification method on the high-power seawater battery model with higher power in seawater galvanic cells and the potential to regenerate the anode using acid zinc solution, addressing the main barrier in utilizing and developing seawater. This method will make seawater a renewable energy source to generate continuous electrical current.

2. MATERIALS AND METHODS

2.1. Materials

This study employs an experimental setup comprising five electrochemical cells. Each cell is constructed using the following materials: seawater as the electrolyte, copper (Cu) and zinc (Zn) plates (7×4×0.05 cm) as electrodes, light-emitting diodes (LEDs) with 5000 mcd 5 V (max) 100 mW as the electrical load, and a 0.02 M $AgNO_3$ solution for deposition processes. Additionally, supporting chemicals include a 1% HNO_3 solution and 96%

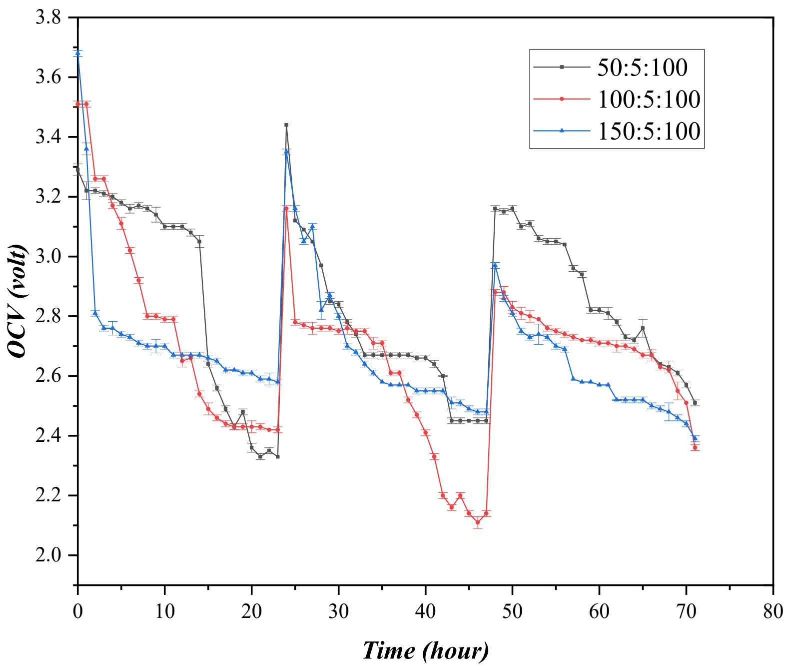

Figure 3. Graph of OCV measurement over 72 h by varying Al_2O_3:carbon:cement ratios.

Table 1. OCV reduction with different separator compositions.

Separator compositions (Al_2O_3:carbon:cement)	OCV (volt)		
	Initial	Final	Difference
50:5:100	3.29	2.51	0.78
100:5:100	3.51	2.36	1.15
150:5:100	3.68	2.39	1.29

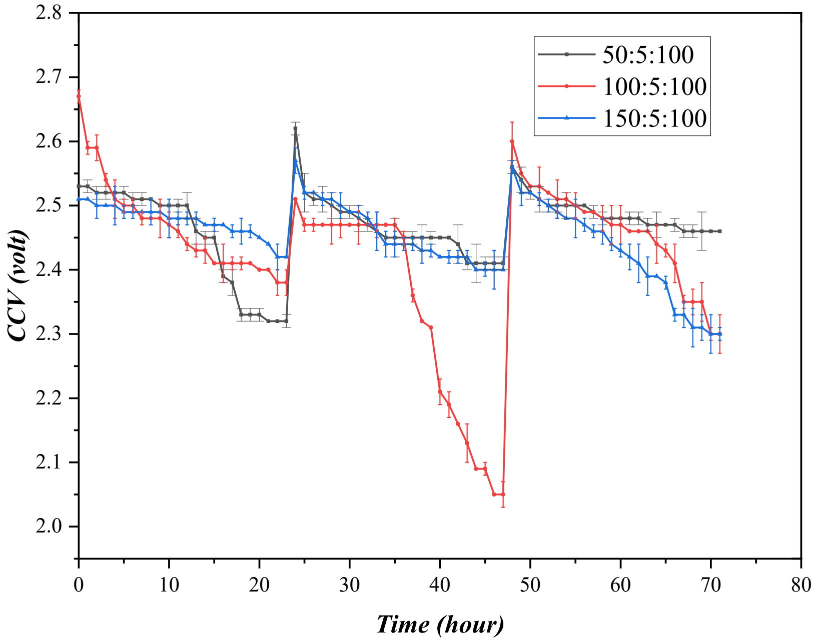

Figure 4. Graph of CCV measurement at 72 h by varying Al_2O_3:carbon:cement ratios.

Tabel 2. CCV with different separator compositions.

Separator compositions (Al_2O_3:carbon:cement)	CCV (volt)		
	Initial	Final	Difference
50:5:100	2.53	2.46	0.07
100:5:100	2.67	2.3	0.37
150:5:100	2.52	2.3	0.22

ethanol for cleaning and pretreatment. The cell assembly further incorpogrates Al_2O_3, carbon powder, and cement as structural or catalytic components. The instruments used are multimeter, digital balance TL series, lux meter, beakers, power supply, and water filtration unit.

2.2. Methods

2.2.1. Preparation of Cu(Ag) Electrodes

Cu(Ag) electrodes for each cell are prepared through an electroplating process using $AgNO_3$ solution in an electrochemical cell with Cu metal as the cathode and carbon rod as the anode. Before electroplating, the Cu metal surface is cleaned with 1% HNO_3 solution to remove dirt from the surface, followed by cleaning with 96% ethanol to remove absorbed HNO_3. Electroplating is carried out at 2 V for 5 min. The Cu electrode coated with electrolyte is removed from the electrochemical cell, rinsed carefully with deionized water, and dried.

2.2.2. Preparation of pH-4 Acid Zinc Solution

First, a pH-5 acid zinc solution is made by mixing 150 g of NH_4Cl, 40 g of $ZnCl_2$ with 1 L of distilled water. A HCl solution is added slowly while continuously monitoring by pH meter until pH 4 is obtained. The pH 4 was selected as it represents a balance point between electrochemical efficiency and the stability of the galvanic cell system [21]. This is based on the consideration that an optimal condition can be achieved, allowing for a high reaction rate, increased current and power, low internal resistance, while corrosion and associated risks remain under control [22]. A pH that is too low (e.g., pH 1) leads to more severe deterioration, while higher pH levels show better resistance to corrosion [23].

2.2.3. Preparation of Separator

Preparation of the separator compositions of Al_2O_3 (alumina + carbon + cement) in ratios of

50:5:100, 100:5:100, and 150:5:100. This composition variations are determined randomly. Seawater is used as the mixing liquid. The preparation involves mixing the variations and stirring until the three materials are combined. The composition is then molded directly into the cell, dried, and left to harden. The separator was made in bulk to ensure consistency in production at one time. After homogenization and hardening, it was cut into 5×10 cm pieces.

2.2.4. Seawater Electrolyte

The seawater electrolyte used is taken from the sea in the Bandar Lampung area. The seawater is first filtered three times with a volume of 110 mL using a water filtration unit. The seawater in the galvanic cell is replaced every 24 h to observe the effect of seawater replacement on electrode surface and electrical characteristics.

2.2.5. Construction of Electrochemical Cell

The electrochemical cell is made of acrylic with dimensions of 8×4×7 cm as shown in Figure 1. For this experiments, 5 cells are assembled in a closed container and connected in series.

2.2.6. Measurement and Data Collection

Measurements are made by arranging 5 galvanic cells in series. Before and after the process, the electrode mass is weighed to determine the corrosion rate of each electrode (Equation 1). Corrosion rate measurements were performed using the Standard Guide for Laboratory Immersion Corrosion Testing of Metals [24], widely used by industry and academia [25]. This method is performed by measuring the mass reduction before and after an electrochemical reaction occurs over a certain time range. Data measured include open circuit voltage (OCV) and close circuit voltage (CCV) (Figure 2), current flowing through 20 parallel super bright LEDs, and light intensity (lux) with a lux meter placed 10 cm from the load. Data were collected over a 72-h period with measurements taken at hourly intervals, consisting of 5 replicates per measurement. This single experimental run was conducted because the electrodes undergo immediate degradation during the discharge process. The internal resistance (R_{in}) (Equation 2) is calculated by first determining the OCV and CCV of the seawater galvanic cell system.

The corrosion rates;

$$r = \frac{K\,m}{\rho\,A\,T} \tag{1}$$

and the internal resistance;

$$R_{in} = \frac{OCV - CCV}{I} \tag{2}$$

where r = corrosion rate (*mm/year*), K = constant ($8.76\times10_4$), ρ = density (g/cm_3), $m = m_0 - m_1$ = (initial mass - final mass) (g), A = surface area (cm_2), Rin = internal resistance (kΩ), OCV = voltage without load (V), CCV =voltage with load (V), and I = current (A).

3. RESULTS AND DISCUSSIONS

3.1. Measurement of the Two-Compartment Seawater Galvanic Cell

The two-compartment galvanic cell is a galvanic cell containing an anode and a cathode separated by a separator made from a compositions of alumina, carbon, cement, and seawater. The electrolyte in the anolyte compartment is filled with pH-4 acid zinc solution and 110 mL of seawater in the catholyte compartment. The separator compositions consist of varying mass ratios for Al_2O_3:carbon:cement, respectively, 50:5:100, 100:5:100, and 150:5:100. The testing was conducted on 5 cells connected in series.

3.2. Measurement of OCV and CCV of the Two-Compartment Seawater Galvanic Cell

Figure 3 shows the OCV measurement graph over 72 h for the two-compartment seawater galvanic cell system. In Figure 3, the voltage at the beginning of the measurement is still optimal. This is due to the clean condition of the electrode surface, allowing the redox reaction between the electrolyte and the electrode surface to occur optimally. Additionally, the high electrolyte content also supports this. In the subsequent process, after 24 h, the OCV gradually decreases. In the following cycles, new peaks in the OCV can be observed at the 25th and 49th hours.

The appearance of new peaks is due to the fact that fresh seawater and acid zinc solution were replaced simultaneously in a short period of time to avoid prolonged exposure to air. The OCV of the 50:5:100 compositions is higher than the initial OCV of the 100:5:100 and 150:5:100 compositions. Although not significant, it increases as the number of cells increases. This indicates that the higher amount of alumina in the separator steadily decreases the OCV of the voltaic cells. The average measurement error OCV is 0.011 V. Table 1 shows a summary of the decrease in OCV of the cells from the beginning to day 3. The final difference is smaller for the 50:5:100 blend than for the other blends.

The graph in Figure 4 shows a CCV measurement over 72 h connected to 20 parallel LEDs. In Figure 4, it can be seen that the voltage measured with load for the 50:5:100 compositions is more stable with a lower voltage drop compared to compositions with a higher amount of Al_2O_3. The average measurement error CCV is 0.012 V. Although some parts of the other compositions exhibit fluctuating values, the results indicate that the voltage stability remains quite good in this compositions, as shown in Table 2.

The voltage required to light each LED ranges from 2–3 V. The measured CCV averages 2.57 V, indicating that the LED does not emit light at maximum brightness; however, in reality, the LED can still emit light, although dimly. In general, some electronic components can still operate under minimal electrical input conditions, but with the consequence that the output is not optimal compared to conditions when the voltage input is in accordance with standard specifications.

The replacement of seawater or acid zinc solution every 24 h results in the electrolyte. Oxygen and dissolved mineral levels in the electrolyte being replenished. This significantly affects the increase in OCV or CCV voltage. The higher the dissolved oxygen content in the electrolyte. the higher the voltage generated by the galvanic cell.

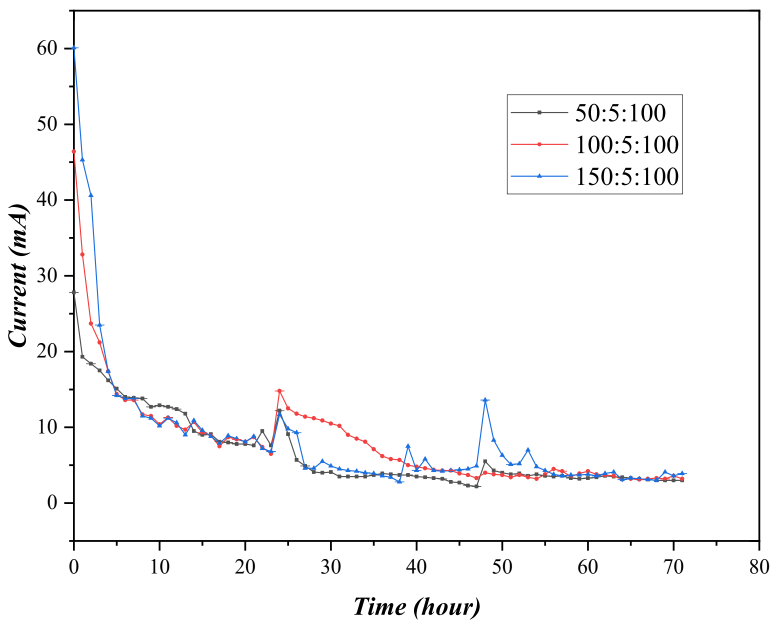

Figure 5. Graph of current measurement in 72 h by varying Al_2O_3:carbon:cement ratios.

Table 3. Summary of current measurement in 72 h.

Separator compositions (Al_2O_3:carbon:cement)	Current (mA)	
	Initial	Final
50:5:100	27.8	3.0
100:5:100	46.4	3.2
150:5:100	60.1	3.9

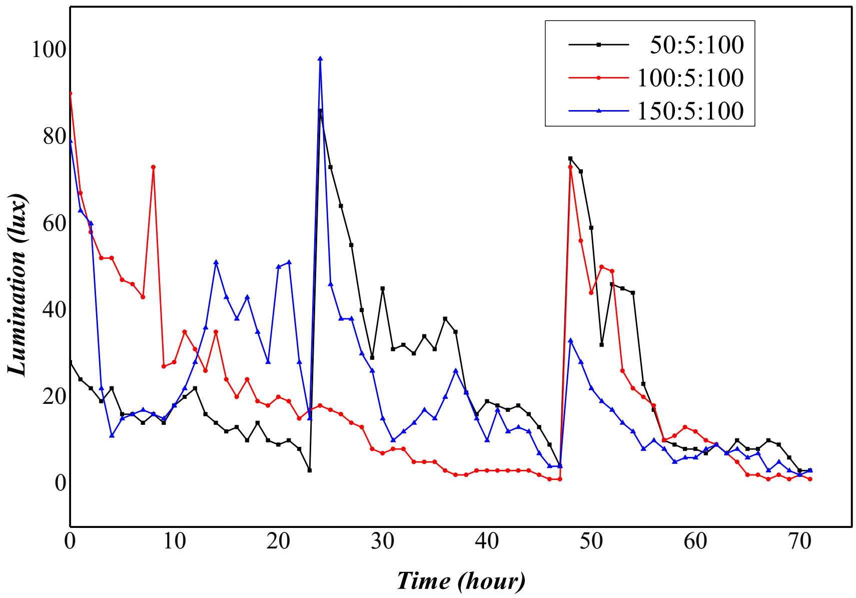

Figure 6. Graph of light intensity measurement at 72 h by varying Al_2O_3: carbon: cement ratios.

Table 4. Summary calculation results of average resistance and power.

Separator Compositions (Al_2O_3:carbon:cement)	R_{in} (KΩ)	Power (mWatt)
50:5:100	0.066	16.922
100:5:100	0.039	20.585
150:5:100	0.035	21.169

3.3. Current Measurement of the Two-Compartment Seawater Galvanic Cell

The current generated by the Cu(Ag)-Zn electrodes using seawater and pH-4 acid zinc solution as the electrolyte can be seen in Figure 5. Figure 5 shows the current graph over 72 h, where it can be observed that the current produced decreases continuously every hour. The observation time and the load used can affect the final current value; the longer the observation period. the smaller the current generated. Figure 5 shows that the 150:5:100 separator compositions produces a higher current value. as the concentration variation used indicates that the more by Al_2O_3 is used. the greater the current generated [26].

Here is the summary of the current values in the two-compartment voltaic cell based on the graph in Figure 5. The current values produced by the voltaic cell can be seen in Table 3. The separator with a higher Al_2O_3 mass variation has higher average current values compared to other mass variations. Therefore. the lower conductivity affects the current and power generated by the voltaic cell. The average measurement error current is 0.004 mA.

3.4. Measurement of Light Intensity in the Two-Compartment Seawater Galvanic Cell

The light intensity data in this study were collected using an AS803 lux meter at a distance of 10 cm from the lamp (20 LEDs arranged in parallel) used. The results of the light intensity measurements for the 50:5:100, 100:5:100, and 150:5:100 separator compositions with pH-4 acid zinc solution and seawater electrolyte over 72 h are presented in Figure 6.

In Figure 6, it is observed that the light intensity for the 150:5:100 variation is higher compared to the 50:5:100 and 100:5:100 variations. This is because the 150:5:100 variation has a higher Al_2O_3 mass in the separator compositions. The light intensity decreases every hour due to the reduced current, as the electrodes experience corrosion caused by the ionization of the electrolyte. The light intensity produced is directly proportional to the current (i); as the current increases, the light intensity will also increase.

3.5. Calculation of Resistance and Power of the Two-Compartment Seawater Galvanic Cell

Based on the OCV and CCV values. calculations can be made to find the average resistance (*Rin*) using Equation (1) and to find the power using Equation (2). Table 4 shows the results of the average resistance and power calculations.

Based on the calculation results. as the Al_2O_3 mass used increases, the power produced also increases. The observation time also affects the power difference. The longer the observation period, the smaller the power difference obtained [26]. The measurement of OCV and CCV indicates that as the amount of alumina increases. the voltaic cell's ability to generate voltage decreases (resistance increases). However. a unique phenomenon occurs when observing the current values verified against the light luminescence produced by the LEDs. The current increases as the amount of Al_2O_3 used increases. Conceptually, this analysis can refer to Randles' impedance model, where in an electrolyte system, there are series and parallel relationships represented by the impedance of each physical variable used. This model helps explain the observed behavior in the system's electrical characteristics [27]. In this section, Al_2O_3 tends to act as a series resistance during voltage measurements and as a parallel resistance during current measurements. To achieve optimal characteristics for a seawater voltaic cell system, it is crucial to balance the internal impedance with the load impedance used. Based on Table 4, the potential power that can be generated by one cubic meter of seawater using the Al_2O_3, carbon, and cement separator compositions with a mass ratio of 150:5:100 is 38.49 W/m³. This result indicates that the power output is higher compared to the single-compartment method.

3.6. Corrosion Rate of Zn Electrodes in the Two-Compartment Seawater Galvanic Cell

The corrosion rate is determined by measuring the mass of the zinc electrodes before and after they are used to generate electricity with a 20 LED load over a 72-h period.

In Table 5, the average corrosion rate of the Zn anode in the pH-4 acid zinc solution is shown for separator mass variations of 50:5:100. 100:5:100. and 150:5:100 over 72 h. The results indicate that as the Al_2O_3 mass increases, the corrosion rate also increases, and vice versa. In this study, the Al_2O_3 mass variation affects the corrosion rate of the Zn anode. In addition to Al_2O_3 mass, seawater electrolyte also contributes to corrosion. The measured corrosion rate in the seawater electrolyte for the anode increases each hour and significantly affects the decrease in electrical power produced by the cell. The resulting corrosion impedes the flow of electrical current. The NaCl content in seawater can accelerate the corrosion rate of Zn [28]. Corrosion cannot be entirely avoided, but its rate can be controlled by using an acid solution as the corrosion rate is significantly lower and the cell's durability in producing electrical energy is improved. Strong acids typically have a pH range of 3–6. According to the previous research [29], the use of pH-4 acid zinc solution resulted in higher corrosion compared to pH 5 and 6. Lower pH values in zinc acid solution improved the electrical characteristics of the cell.

The long-term effect of anode corrosion can lead to detrimental consequences, including a decrease in cell efficiency, an increase in internal resistance causing electrode surface passivation, contamination of the electrolyte when it becomes saturated, microstructural changes that lead to

Table 5. Average corrosion rate of Zn with pH-4 acid zinc solution after 72 h.

Separator Compositions (Al_2O_3:carbon:cement)	Corrotion Rate (mm/year)
50:5:100	0.276
100:5:100	0.415
150:5:100	0.510

Table 6. Comparison of the characteristics of single-compartment and two-compartment galvanic cells using separators and acid zinc solution.

Characteristics	Single-Compartment	Two-Compartment
V_{OCV} (V)	4.3283	3.4933
V_{CCV} (V)	2.0292	2.5733
I (mA)	0.4567	44.7667
R_{in} (kΩ)	1.1076	0.0467
P (mWatt)	3.7175	19.5587
Zn corrosion rate (mm/year)	0.486	0.4003

cracking, and an imbalance in electrochemical potential. Continuous corrosion of the anode can be prevented by regenerating the anode. In future research, Zn regeneration will be conducted using acid zinc solution through half-cell electrolysis between the separator and the anode. In general, the mineral content of seawater is dominated by NaCl, along with other minerals. Therefore, seawater sources from Bandar Lampung have the potential to be developed as seawater batteries. In some locations with different geographical conditions, seawater composition may vary, leading to differences in cell performance. Variations in mineral composition in seawater can influence electrolyte conductivity, output voltage, electrode lifespan, and electrochemical reaction efficiency.

3.7. Comparison of Two-Compartment (Acid Zinc Solution) and Single-Compartment (Non Acid Zinc Solution) with Separator

In this study the comparison was made between a two-compartment cell using acid zinc and a single -compartment cell (without separator) using non-acid zinc solution. The two-compartment cell setup included electrodes Cu(Ag)-Zn with an acid zinc solution as electrolyte. For the single-compartment cell, which did not use a separator the setup consisted of the same electrodes with seawater as the electrolyte. The single-compartment cell was tested with 20 cells and a load of 3-Watt 12-V LEDs [9]. Then, with equal comparison calculations (dividing the data by four and calculating the real load), Table 6 shows the characteristics comparison between the single-compartment system and the two-compartment system using a separator and acid zinc solution (using the average data from Table 4). Table 6 shows significant differences in current, resistance, and power output between the single-compartment and two-compartment systems. The results indicate current increased by up to 97.81 times, power increased by 5.25 times, and resistance reduced by 95.7%.

There is no significant difference in the Zn corrosion rate, meaning the cell does not become more prone to degradation compared to the single-compartment system. However, it can generate higher power output. The acid zinc solution does not significantly affect the OCV as this is determined by the electrode pair arrangement in the voltaic series. However, the power output can increase due to reduced cell resistance and enhanced solution conductivity. In galvanic cells, resistance is influenced by separator porosity [30] [31], electrode thickness, and surface area, as well as reaction products forming passivation layers on electrode surfaces. Solution conductivity depends on ion concentration and pH level. Thus, it can be stated that the pH-4 acid zinc solution contributes significantly to reducing internal resistance, leading to a higher current output.

4. CONCLUSIONS

The use of acid zinc solution significantly enhances the electrical characteristics in terms of current, resistance, and power output. There is an increase of up to 97.81 times in current, 5.25 times in power, and a reduction in resistance by 95.7%. However, there is no significant change in the corrosion rate of Zn. The pH-4 acid zinc solution contributes significantly to reducing internal resistance, which results in higher current output. A separator composition with a higher amount of alumina has greater conductivity compared to a separator compositions with a lower amount of Al_2O_3.

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Conflicts of Interest

The authors declare no conflict of interest.

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