Research Article

Electrochemical Characteristics of Ambarella Peel Waste as Liquid Electrolyte for Zn-Cu Biobattery

Marcelinus Christwardana*
Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University, Semarang, Indonesia
Master Program of Energy, School of Postgraduate Studies, Diponegoro University, Semarang, Indonesia
Research Collaboration Center for Electrochemistry, BRIN-Diponegoro University, Indonesia

Renanda Aprilia Putri Pramudita and Ngadiwiyana Ngadiwiyana
Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University, Semarang, Indonesia

* Corresponding author. E-mail: marcelinus@lecturer.undip.ac.id DOI: 10.14416/j.asep.2024.11.001
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Abstract

This study focuses on the electrochemical characterization of Zn-Cu bio-battery cells utilizing electrolytes derived from ambarella peel waste. The primary objectives are to determine the half-cell and full-cell characteristics of these bio-batteries at various concentration ratios and to identify the optimal concentration ratio for maximum performance. Cyclic voltammetry analysis of the half-cells revealed an oxidation peak at 0.5 V vs Ag/AgCl, corresponding to the conversion of uronic acid to aldaric acid. Additionally, two reduction peaks were observed: hydrogen ion reduction to H_2 at 0 V vs Ag/AgCl and water reduction at –0.42 V vs Ag/AgCl. The rate-determining step analysis indicated that the redox reactions in the ambarella peel electrolyte solution were surface reactions. The highest rate constant (k_s) of $0.722 \pm 0.05\ s^{-1}$ was observed at a 1:2 concentration ratio. This ratio also resulted in the highest battery capacity of 0.0816 mAh and the maximum power density of 16.13 mW/m^2. The study concluded that the 1:2 concentration ratio of ambarella peel waste electrolyte solution is optimal, outperforming the 1:1 and 1:3 ratios in terms of battery capacity and power density.

Keywords: Bio-battery, Bioenergy, Biomass, Ionization degree waste-to-energy, Zn-Cu

1 Introduction

Fossil energy is currently the primary energy source, but its availability is steadily diminishing due to its constant and extensive utilization. Furthermore, fossil energy is finite and cannot be replenished [1]. Concurrently, the task of locating fossil fuel reserves will become progressively challenging, while the need for energy will rise in tandem with the expanding population. The disparity between the significant demand for energy and the limited availability of fossil fuel resources can lead to an energy crisis. Consequently, it is imperative to explore renewable energy sources or alternative energy options to mitigate this issue [2]. Alternative energy refers to energy derived from natural sources and subsequently transformed into renewable energy [3]. A battery is a form of alternative energy. Batteries serve as chemical energy storage devices that are subsequently transformed into electrical energy. An example of such a technology is a bio-battery, which is an environmentally benign battery composed of organic components [4]. Fruits and vegetables, particularly their peels, can serve as a battery electrolyte, making them a viable organic material for this purpose. The buildup of vegetable and fruit peels can have a negative influence on the environment if not managed effectively. Therefore, it is crucial to find an efficient method to address this issue. One such concept is waste-to-energy, which involves using waste as a source of energy [5]. So *et al*., introduced bio-batteries in a study, utilizing energy sources derived from organic materials such as carbohydrates, amino acids, and enzymes [6]. Siddiqui and Pathrikar asserted that bio-batteries, which employ enzymes and microorganisms to convert glucose into hydrogen ions and electrons, are both environmentally friendly and renewable energy storage devices [7]. An electrolyte source was created by combining ambarella fruit and banana peels. The findings indicated that the optimal concentration was a mixture of 25% ambarella fruit and 75% banana peels [8]. This mixture, when fermented for 24 h, generated a voltage of 3.84 V and a current of 2.13 mA. The study conducted by Hussain *et al.*, investigated the use of electroactive antioxidants derived from vegetable waste to create rechargeable bio-battery cells [9]. The findings revealed that applying heat or cooking vegetables, as well as optimizing the pH of vegetable juice, can enhance the voltage output of the bio-battery. Furthermore, the combination of radish and cactus vegetable waste yielded the highest voltage among the various vegetable waste combinations. In another study, oranges and orange peels were utilized as natural active components in electrolyte solutions for bio-batteries [10]. The study demonstrated that changes in volume can impact the voltage measurements, with a direct correlation between pH levels and voltage production. Specifically, lower pH levels resulted in higher voltage output. In a study by Togibasa *et al.*, bio-batteries utilizing tropical almond paste were examined [3]. The researchers found that tropical almond demonstrated an open circuit voltage (OCV) of 0.98 ± 0.09 V and a power output of 0.25 mW. The power curve analysis indicated that the glucose content of the tropical almond paste was responsible for generating the observed voltage.

Ambarella peel is one of the fruit wastes that can potentially be used as a raw material for making bio-battery electrolytes because it has acidic properties from the organic acids that make it up, including uronic acid, titrated acid, and ascorbic acid [11]. Acids are electrical conductors because acids in water solvents can be ionized to produce anions and cations that play a role in electricity or are also known as electrolyte solutions [12]. The higher the acid content, the lower the pH of the solution, and the greater the electric current produced, and vice versa [13]. The concentration of the solution affects the amount of substrate in it, including the amount of acid, the higher the concentration of the solution, the greater the amount of dissolved acid. This can affect the performance of the electrolyte solution as a bio-battery material, therefore in this study, variations in the concentration ratio of the electrolyte solution of ambarella peel waste were carried out to determine its effect on bio-battery performance. Zn-Cu batteries are a type of battery commonly used in the automotive industry, aerospace industry, and energy storage, this is because Zn-Cu batteries have a high capacity, including renewable energy, good cycle stability, and strong anodes [14]. In general, Zn-Cu type batteries have 3 types [15]. Zn-Cu type 1 batteries are Zn-Cu batteries that use strong acid solutions and without a separating membrane. In type 2, the Zn-Cu electrodes are separate and there is a salt bridge, and in type 3, the Zn-Cu battery is rechargeable. The use of Zn-Cu as an electrode because it has high conductivity, is affordable, and is easy to obtain [16]. In this study, we will conduct electrochemical characterization of bio-battery cells using Zn-Cu electrode type batteries. Zn-Cu type 1 batteries with electrolytes from ambarella peel waste, where variations in the concentration ratio of the electrolyte solution will be carried out. Electrochemical characterization was carried out by half-cell analysis including cyclic voltammetry (CV), rate determining step (RDS), electron transfer rate constant (k_s), and full-cell analysis including measurement of maximum power density and battery capacity, as well as additional analysis, namely measurement of pH and H_2 solution. The use of ambarella peel as a raw material for making electrolytes because ambarella contains organic acids that have the potential to produce electric current. It is hoped that this research on ambarella peel waste as an electrolyte can be used as an alternative energy in Zn-Cu bio-batteries. There are several objectives of this study. First, to obtain half-cell characteristics of Zn-Cu bio-batteries that use electrolytes from ambarella peel waste at various concentration ratio variations. Second, to obtain full-cell characteristics of Zn-Cu bio-batteries that use electrolytes from ambarella peel waste at various concentration ratio variations. Third, to obtain the best concentration ratio variation of ambarella peel waste electrolyte solution for Zn-Cu bio-battery cells.

This finding has substantial potential to contribute to the advancement of sustainable energy solutions. The study aims to determine the ideal concentration ratio of ambarella peel waste electrolyte, which could lead to the development of bio-batteries that are both more efficient and environmentally beneficial. These findings have the potential to be expanded and used on a larger scale in industrial settings, providing a sustainable substitute for conventional energy storage systems. These innovations have the potential to meet the increasing need for renewable energy and help decrease the environmental degradation caused by the disposal of fruit waste. In the larger drive to shift from fossil fuels to renewable energy sources, this discovery could have a crucial impact, contributing to both environmental sustainability and energy security.

2 Materials and Method

2.1 *Preparation of ambarella peel extract*

Ambarella peel is obtained from the fruit that exhibits green, firm, and fully mature qualities. The ambarella peel is cleansed using purified water and subsequently dried at a temperature of 70 °C utilizing a drier [17]. The dehydrated ambarella peel is pulverized into a fine powder using a blender. Then 2 g of ambarella peel powder was immersed in an ethanol solvent, allowing it to sit for 20 min, followed by filtration using filter paper. The strained liquid is kept for phenol and flavonoid examinations. For tannin analysis, 2 g of ambarella peel powders are dissolved in 100 mL of distilled water and the resulting solution is filtered using filter paper. The filtrate that has been passed through a filter is kept for further testing.

2.2 *Phytochemicals screening*

2.2.1 Phenolic test

The qualitative phenolic test is conducted by introducing 3–4 droplets of a 1% solution of $FeCl_3$ to the ethanol extract derived from ambarella peel [18]. A positive test is confirmed by the creation of a solution that appears blackish green.

2.2.2 Flavonoid test

The qualitative flavonoid test is conducted by introducing 3–4 drops of sodium hydroxide (NaOH) solution [19]. A good result for flavonoids is indicated when the extract solution changes color to yellow-red.

2.2.3 Tannin Test

The qualitative tannin test involves adding a small amount of 1% $FeCl_3$ to the aquadest extract of ambarella peel [20]. A blackish green solution development signifies the existence of tannin components in the extract.

2.3 *FTIR analysis measurement*

The extract of ambarella peel samples was subjected to FTIR analysis within the wave number range of 4000–400 cm^{-1}. The ambarella peel extract was subjected to FTIR analysis to identify the functional groups present in the chemical components.

2.4 *Total acid analysis measurement*

An acid-base titration is employed as an approach for determining the overall acidity in the extracted sample. The acid being titrated reveals the quantity of acid present in the sample. The ambarella peel was pulverized with a blender, using 187.5 mL of distilled water, resulting in a total weight of 62.5 g. Next, the solution was passed through a filter to separate and collect the filtrate. 20 mL of the filtered filtrate was transferred into an Erlenmeyer flask and 2–3 drops of phenolphthalein (PP) indicator solution were added for further titration. A standard solution of 0.1 N NaOH was prepared and transferred into a burette [21]. The volume of the solution was then measured and recorded. The titration process was continued until the point of equivalence was achieved, which was indicated by a noticeable shift in color. The recorded volume of the standard solution of 0.1 N NaOH was used to determine the titrated total acid.

2.5 *Preparation of electrolyte solution*

The electrolyte solution is produced by utilizing ambarella peel waste and aquadest solvent. The ambarella peel is measured based on the mass ratio of ambarella peel to aquadest, which adjusted to be 1:1, 1:2, or 1:3. The total mass of the mixture is 250 grams. In addition, the ambarella peel and aquadest are blended together until they form a smooth and uniform mixture. The outcomes of the homogeneous solution are transferred into a 250 mL glass beaker for subsequent examination in both half cells and complete cells.

2.6 *Analysis of half-cells*

2.6.1 Half-cell circuit preparation

Half-cell analysis is conducted to ascertain the properties of the electrolyte solution. The electrolyte solution is prepared by incorporating a stainless-steel comparison electrode, an Ag/AgCl reference electrode, and a glassy carbon working electrode.

Next, the electrode is securely attached to the potentiostat using a clamp, and the potentiostat is then connected to a laptop.

2.6.2 Cyclic voltammetry measurement

Cyclic voltammetry (CV) analysis is performed to ascertain the electrochemical potential for reduction and oxidation in the electrolyte. The analysis is conducted using a potentiostat rodeostat set at a scan window of –1 V to 1 V, with a scan rate varying from 100 to 1600 mV/s.

2.6.3 Measurement of the rate determining step

The objective of rate determining step (RDS) analysis is to ascertain the nature of the reaction, whether it is a surface reaction or a diffusion reaction, based on the shape of the resulting curve. The analysis was conducted by adjusting the scan window from –1 V to 1 V. The scan rate ranged from 100 mV/s to 1600 mV/s, resulting in 16 data points for each redox peak. Then, a curve between the current density and the scan rate was made.

2.6.4 Electron transfer rate constant measurement

The objective of analyzing the electron transfer rate constant (k_s) is to ascertain the velocity at which electrons are transferred from the electrolyte solution to the electrode. The study was conducted by configuring the scan window from –1 V to 1 V. The scan rate ranged from 100 mV/s to 1600 mV/s, resulting in 16 data points for each redox peak. Finally, the curve between the potential and the log of the scan rate was made.

2.7 *Full cell analysis*

2.7.1 Full cell circuit preparation

Full cell analysis is conducted to thoroughly examine and describe the battery cell in its entirety. Copper electrodes are introduced as positive cathodes, whereas zinc is used as negative anodes in the prepared electrolyte solution, as shown in Figure 1. Next, the solution is purged with nitrogen gas and sealed with plastic wrap. In addition, the electrodes that have been inserted are linked to a multimeter via alligator clips.

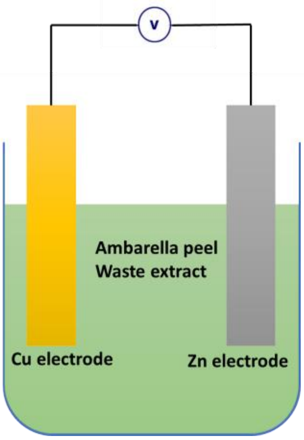

Figure 1: Schematic diagram of Zn-Cu biobattery cell.

2.7.2 Measurement of battery capacity, pH, and H_2

The objective of the battery capacity study is to quantify the capacity of the bio-battery. The objective of pH and H_2 measurements is to ascertain the fluctuations in pH and H_2 levels within the bio-battery cell throughout the incubation period. Cu and Zn electrodes are introduced into the prepared electrolyte solution. Next, the solution is purged with nitrogen gas and sealed with plastic wrap. In addition, the electrodes that have been implanted are linked to an external resistance of 10 MΩ and subsequently connected to a multimeter using crocodile clips. Measurements are conducted daily until the current reaches a steady state. Every day, pH and H_2 levels are measured using a 4 in 1 water tester, which also allows for the measurement of battery capacity.

2.7.3 Maximum power density

The objective of the greatest power density is to establish the correlation between electrochemical potential and the power generated by a bio-battery. Cu and Zn electrodes are immersed into the prepared electrolyte solution. Next, the solution is purged with nitrogen gas and sealed with plastic wrap. Moreover, the electrodes that have been inserted are linked to a resistor and multimeter through the utilization of crocodile clips. The external resistance can be adjusted within the range of 10 Ω to 10 MΩ. Stable voltage analysis is conducted at each site. The value of current (I) is calculated using the formula $I = V / R$, where V represents voltage and R represents resistance. Additionally, the power (P) can be determined by multiplying the voltage (V) by the current (I), using the formula P = V × I. The relationship between the variables I and P follows a power curve.

3 Result and Discussion

3.1 *Characterization of ambarella peel chemical content*

3.1.1 Phytochemical screening characteristics

Phytochemical screening is a characterization method used in this work to identify the specific chemicals present in the extract of ambarella peel. The conducted phytochemical screening included a phenol test, flavonoid test, and tannin test. The acquired results demonstrated a shift in the solution's color to a dark greenish hue, indicating the presence of phenolic chemicals in the extract of ambarella peel. The color complex arises from the chemical reaction between phenol and $FeCl_3$ which results iron(III) phenoxide or iron(III) phenol complex which gives a color ranging from yellow to dark green [18]. The results indicated a positive test for the existence of flavonoid chemicals, resulting in the creation of a yellow solution. The yellow hue is a result of the chemical reaction between NaOH and flavonoids, leading to the formation of a complex molecule or acetophenone [22]. During the tannin test, the addition of $FeCl_3$ to the filtrate resulted in the creation of a solution that appeared blackish green. This observation confirms the presence of tannin components in the filtrate. The color complex is created through the reaction between tannin or polyphenol chemicals and $FeCl_3$ [23].

The qualitative analysis identified the existence of phenols, which are recognized for their antioxidant characteristics, underscoring the significance of maintaining a suitable balance of these compounds to ensure stability and conductivity. Furthermore, the presence of flavonoids was identified, which enhances the antioxidant capability of the electrolyte. It is essential to maintain adequate quantities of flavonoids to ensure optimal performance. Tannins were also detected, and their content is acknowledged as a crucial component impacting the stability and conductivity of the electrolyte. An overabundance or insufficiency of these phytochemicals might have a substantial effect on the performance of biobatteries. High levels may result in improved stability but decreased conductivity, whereas low levels could enhance conductivity but jeopardize stability and overall performance.

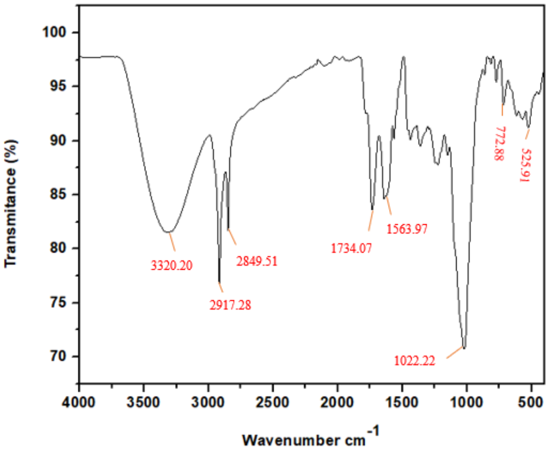

Figure 2: IR spectrum of ambarella peel extract.

3.1.2 FTIR analysis

The IR spectrum data depicted in Figure 2 displays clear absorption bands that correlate to important functional groups found in the ambarella peel extract, emphasizing its abundant chemical composition. A distinctive absorption band at 3320 cm^{-1} is seen, indicating the presence of the O-H stretching vibration. This is a characteristic feature of phenolic substances, carboxylic acids, uronic acids, and ascorbic acid. This indicates a significant abundance of chemicals in the extract that possess hydroxyl groups. The absorption band of about 1734 cm^{-1} corresponds to the C=O stretching vibration, which is a distinctive feature of carbonyl groups present in carboxylic acids, uronic acids, ascorbic acid, and flavonoids. This indicates the existence of molecules that contain carbonyl groups, which are essential for the biological action of the extract. The absorption peak observed at 1641 cm^{-1} is caused by the stretching vibration of the C=C bond, a characteristic feature often present in phenolic compounds, tannins, and ascorbic acid. The presence of conjugated double bonds inside the aromatic rings of these chemicals shows their contribution to the antioxidant activities of the extract. The absorption bands observed at 2917 cm^{-1} and 2849 cm^{-1} correspond to the stretching vibrations of C-H bonds, which are specifically related to uronic acid and ascorbic acid. The existence of aliphatic carbon chains inside the extract is indicated by these bands, which contribute to its structural complexity. The absorption bands observed at 1148 cm^{-1} and 1022 cm^{-1} indicate the presence of C-O stretching vibrations, which are specific to phenolic chemicals, flavonoids, tannins, uronic acids, and ascorbic acid. The presence of ether and ester functional groups in these bands indicates that the extract has the potential to be an effective electrolyte with strong electrochemical activity, thanks to its acidic character. In the research of Barros *et al.*, the absorption bands formed at 1100 cm^{-1} and 1018 cm^{-1} showed the intensity of the presence of uronic acid compounds [24]. The IR spectrum analysis of ambarella peel extract reveals the presence of several functional groups, including O-H, C=O, C=C, C-H, and C-O. These functional groups are related with phenolic chemicals, carboxylic acids, uronic acids, ascorbic acid, flavonoids, and tannins. These chemicals are essential for determining the extract's electrochemical characteristics, which makes it a highly attractive possibility for use in bioelectrochemistry applications.

3.1.3 Total acid analysis

An acid titration assay was conducted to determine the quantity of acid present in the ambarella peel extract. The acid-base titration method was employed, with 0.1 N NaOH serving as the titrant to identify the presence of acid in the sample solution. Furthermore, a phenolphthalein indicator was employed as a means of detecting the conclusion of the titration process, as evidenced by a noticeable alteration in color inside the substance being analyzed. Since the original color of the ambarella peel waste is yellow, the pink color at the titration end point changed the color to become cloudy dark yellow-greenish, as shown in Figure 3. The analyte solution exhibited a chromatic alteration throughout titration, signifying the conclusion of the titration process. According to the titration results, the concentration of acid in the analyte solution was determined to be 26.6 g/L.

3.2 Half cell characteristics

3.2.1 CV analysis

The results indicate that, in Figure 4, the cyclic voltammetry examination of the electrolyte solution of ambarella peel waste at a scan rate of 100 mV/s leads to the formation of reduction and oxidation peaks. According to Figure 4, when the concentration ratio is 1:1, an oxidation peak (a) and a reduction peak (b) and (c) are observed. The peak observed at 0.56 V vs Ag/AgCl is designated as the oxidation peak. This suggests that the uronic acid, an organic acid present in the electrolyte solution of ambarella peel waste, undergoes oxidation [25]. Furthermore, the cyclic voltammetry study of the ambarella peel electrolyte, using a 1:1 ratio, reveals the presence of a reduction peak, namely peak (b) at 0.2 V vs Ag/AgCl. This peak corresponds to the reduction potential of hydrogen ions (H^+) to H_2 [26]. The peak observed at –0.60 V vs. Ag/AgCl is identified as the reduction reaction of O_2 [27]. Figure 5 demonstrates the inclusion of H_2 gas in the CV analysis of ambarella peel electrolyte, with a concentration ratio of 1:1.

Figure 3: Color changes in ambarella peel waste before and after the titration endpoint.

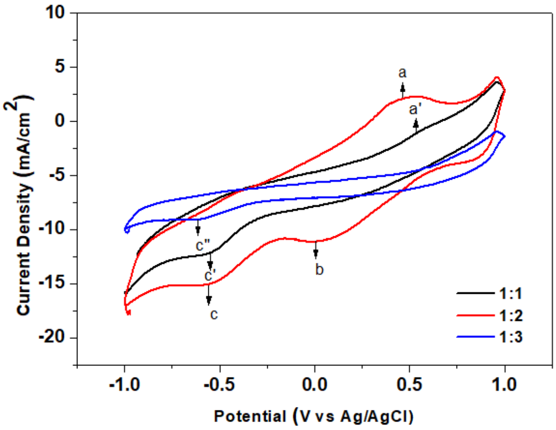

Figure 4: Cyclic voltammetry spectra of ambarella peel extract as electrolyte.

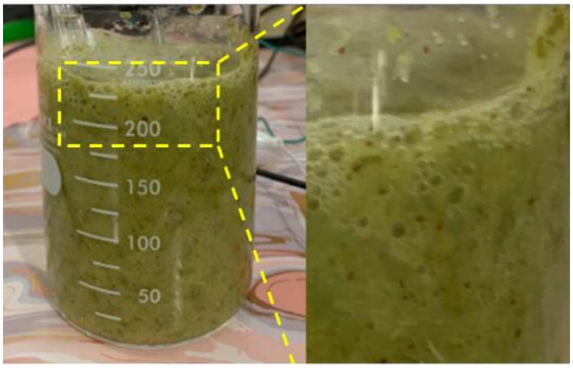

Figure 5: H_2 bubbles in biobattery cells with ambarella peel electrolyte.

The CV examination of the ambarella peel electrolyte solution with a 1:2 concentration ratio and a scanning rate of 100 mV/s resulted in the detection of three peaks. These peaks include one oxidation peak (a') and two reduction peaks (b') and (c'). At a voltage of 0.54 V compared to Ag/AgCl, an oxidation peak was observed in the ambarella peel waste electrolyte solution. This peak suggests that the uronic acid, an organic acid present in the solution, experienced oxidation at the specific potential value [25]. The peak at a potential value of 0 V vs Ag/AgCl was identified as the hydrogen ion (H^+) response to H_2. The peak observed at –0.61 V versus Ag/AgCl was determined to be the reduction reaction of H_2O. The concentration ratio of 1:3 ambarella peel electrolyte solution, with a scan rate of 100 mV/s, exhibits the formation of three peaks. One of these peaks, observed at 0.5 V vs Ag/AgCl, corresponds to the oxidation of organic acids present in the ambarella peel waste electrolyte solution, specifically uronic acid. The reduction reaction is depicted by peaks (b”) and (c”). The peak (b”) represents the maximum value obtained from the reduction reaction of hydrogen ions (H^+) to H_2 gas. The peak at –0.63 V represents the potential value of the reduction reaction of H_2O. Using CV analysis at a scan rate of 100 mV/s, the identification findings show that the electrolyte solution containing ambarella peel at varied concentration ratios exhibits three peaks at the same potential. At a concentration ratio of 1:2, the current density is more positive under oxidation conditions and more negative under reduction conditions, compared to concentration ratios of 1:1 and 1:3. According to the cyclic voltammetry study, it is evident that the redox reaction activity is greater at a concentration ratio of 1:2 compared to concentration ratios of 1:1 and 1:3.

This analysis provides insights into the redox reaction occurring in the electrolyte solution. Furthermore, the electron double layer on the concentration ratio cv graph of 1:2 has a greater magnitude compared to concentration ratios of 1:1 and 1:2. This significant electron double layer results in a higher capacitance. According to Figure 4, the capacitance can be determined. The concentration ratios of 1:1, 1:2, and 1:3 correspond to capacitance values of 0.00039 F/g, 0.00101 F/g, and 0.00019 F/g, respectively. The relationship between capacitance and battery capacity is directly proportional. Therefore, the electrolyte solution of ambarella peel with a concentration ratio of 1:2 has the ability to generate the highest capacity. The cyclic voltammetry examination of the electrolyte solution derived from ambarella peel waste revealed that the concentration ratio of 1:2 exhibited superior electrochemical properties in comparison to the concentration ratios of 1:1 and 1:3.

3.2.2 RDS Analysis

The rate determining step is a method used to identify the nature of a reaction, namely whether it is a surface reaction or a diffusion reaction. The rate determining step graph illustrates the correlation between the scan rate and the current density. In order to conduct the rate determining step analysis, it is necessary to get an electrolyte CV profile using a scan rate ranging from 100 to 1600 mV/s (as shown in Figure 6(a)–(c)).

This profile is then used to establish the relationship between the scan rate and the current density, as depicted in Figure 7(a)–(c). As the scan rate increases, the reduction-oxidation peak on the voltammetry graph becomes more pronounced. A linear relationship indicates that the reduction-oxidation reaction taking place is non-diffusion-controlled, also known as a surface reaction. This type of reaction occurs specifically on the electrode surface [28]. The reason for this phenomenon is that electrons undergo reactions on the surface of the electrode without the need for diffusion. As a result, at every scan rate, the current density measured reaches its maximum value, resulting in the formation of a linear line.

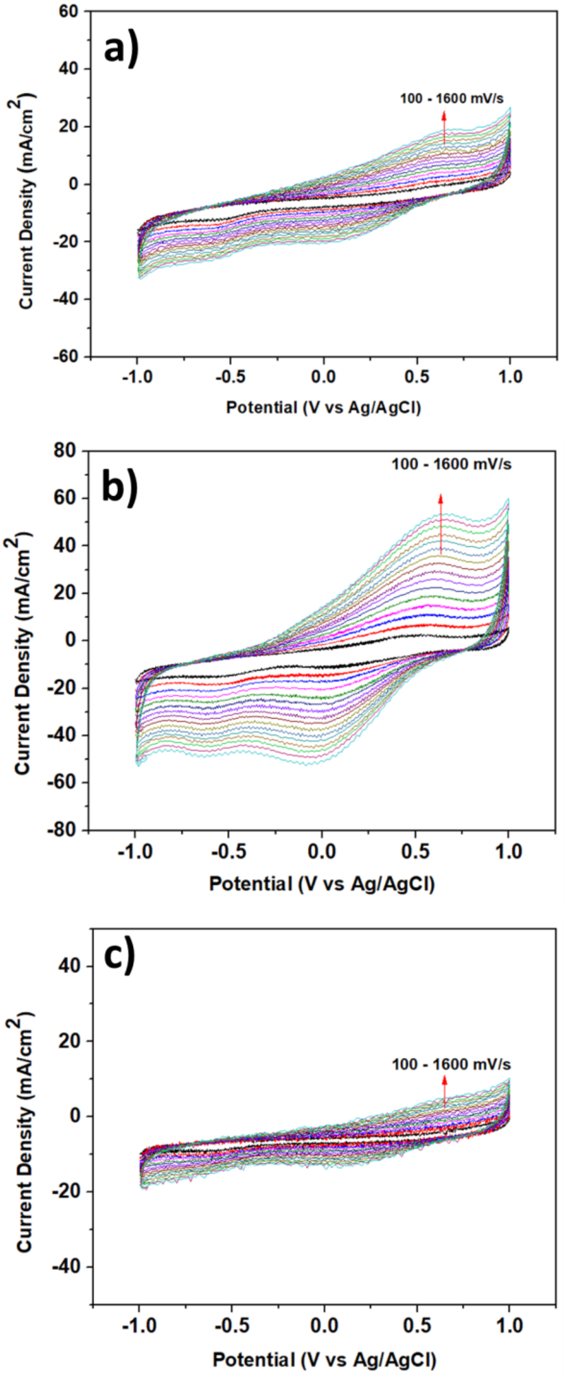

Figure 6: Increase in scanning rate of CV in biobattery with ambarella peel concentration ratio a) 1:1 b) 1:2 c) 1:3.

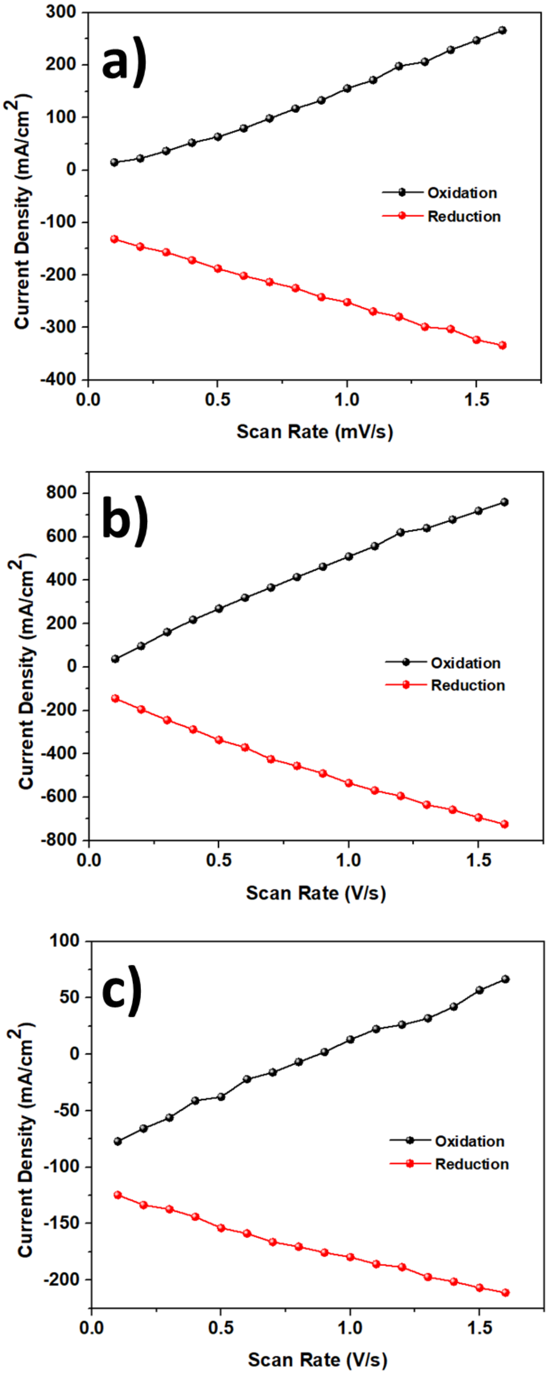

Figure 7: Rate determining step curve for ambarella peel concentration ratio a) 1:1 b) 1:2 c) 1:3.

3.2.3 Electron transfer rate constant analysis

The electron transfer rate constant (k_s) is measured to quantify the speed at which electrons move from the electrolyte solution to the surface of the electrode. The Laviron equation can be utilized to get the k_s [29]. The k_s value is derived from the peak points on the cyclic voltammetry curve by fitting them to a linear equation and obtaining the slope value (Figure 8(a)–(c)). The slope value is utilized to get the value of α, which is subsequently inserted into the Laviron equation. The Laviron equation yields the k_s values for electrolyte solutions with ratios of 1:1, 1:2, and 1:3 as 0.722 ± 0.05 s^{-1}, 1.231 ± 0.07 s^{-1}, and 0.474 ± 0.005 s^{-1}, respectively. Based on the k_s value, it can be concluded that the electrolyte solution with a ratio of 1:2 exhibits the highest performance as an electron transfer electrolyte solution. The k_s value represents the rate at which electrons are transferred to the electrode. Therefore, a solution with a higher concentration of ions will result in a higher k_s value. Nevertheless, in this investigation, the k_s value was higher at a concentration ratio of 1:2 compared to a concentration ratio of 1:1, indicating a greater potential for ionization of organic acid. The higher k_s value at a concentration ratio of 1:2 compared to a concentration of 1:1 can be attributed to the decrease in ion mobility caused by the high concentration of the solution. This decrease in mobility leads to a decrease in the conductivity of the solution. As the concentration of the solution increases, the distance between ions in the solution decreases, resulting in the formation of non-conductive ion pairs and a decrease in the number of free ions that contribute to the conductivity of the solution [30]. Furthermore, excessively concentrated solutions exhibit a high viscosity, which hinders the suppression of ion movement and consequently reduces conductivity [31]. The k_s value is similar to the results obtained from cyclic voltammetry and Rate determining step analysis, indicating that the concentration ratio of 1:2 yields the most favorable electrochemical characteristics as an electrolyte material for bio-battery cells.

3.3 *Full cell characteristics*

3.3.1 Battery Capacity, pH Test, and H_2

The goal of evaluating battery capacity is to assess the battery's performance or capacity by comparing its concentration fluctuations with a ratio of 1:1, 1:2, and 1:3. The bio-battery's capacity is determined by observing its reaction to increasing load until the current stabilizes at a constant value or reaches 0 V. As depicted in Figure 8, the current in the bio-battery cell diminishes progressively over time until it stabilizes at a consistent level.

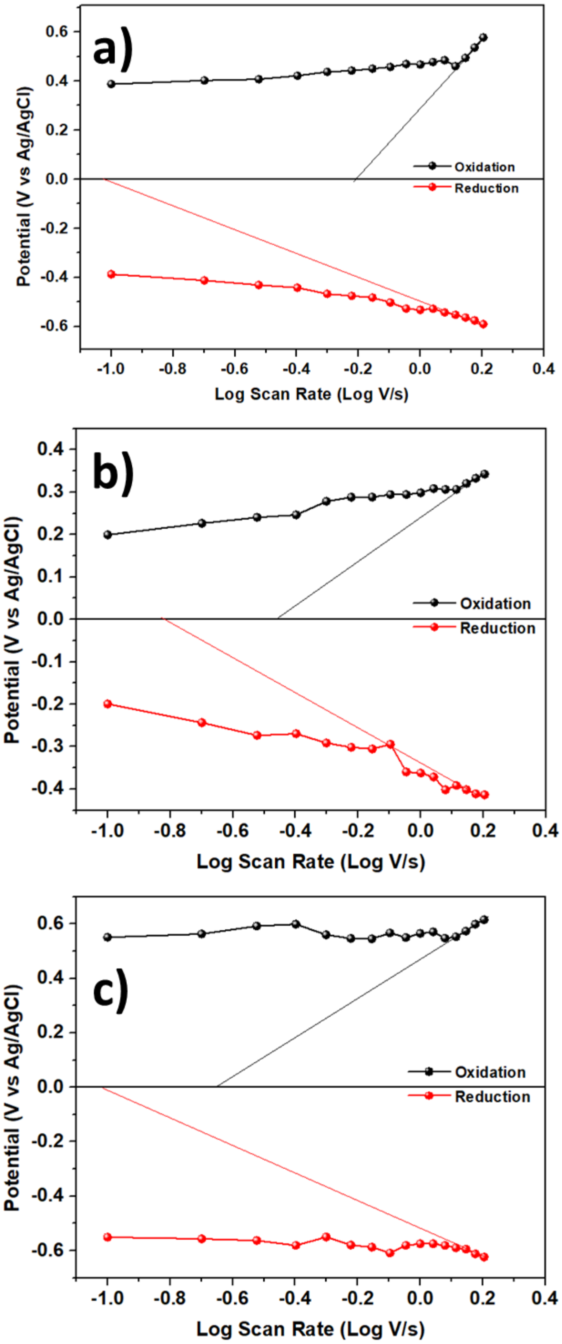

Figure 8: Laviron curve on biobattery with ambarella peel electrolyte concentration ratio a) 1:1, b) 1:2, c) 1:3.

Figure 9 demonstrates that when the ratio is 1:1, the voltage remains constant starting from the 5th day. However, when the concentration ratio is 1:2, the voltage stabilizes on the 15th day, and for a concentration ratio of 1:3, it stabilizes on the 6th day. This indicates that the 1:2 concentration ratio requires more time to achieve a stable voltage, resulting in a longer duration of usage compared to electrolyte solutions with concentration ratios of 1:1 and 1:3. The measured capacity of the 1:2 battery is 0.0816 milliampere-hours (mAh), while the capacity of the 1:1 concentration battery is 0.0048 mAh and the 1:3 concentration battery has a capacity of 0.00432 milliampere-hours (mAh). The capacity measurements on a fully charged cell yield similar results to the electrochemical characterization performed in the examination of a half-cell. In this analysis, the concentration ratio of 1:2 exhibits the most favorable electrochemical properties. Nevertheless, the present intensity of the ambarella peel, measuring 0.75 µA, falls short of the findings from Swartling with the value of 154 µA in a Zn-Cu bio-battery powered by lemon electrolyte [32]. Nevertheless, it surpasses the findings of the study conducted by Wang *et. al.*, which employed an Mg-Mo bio-battery utilizing fruit gelatin electrolyte and had a capacity of 2.9 µAh/cm^2 [33].

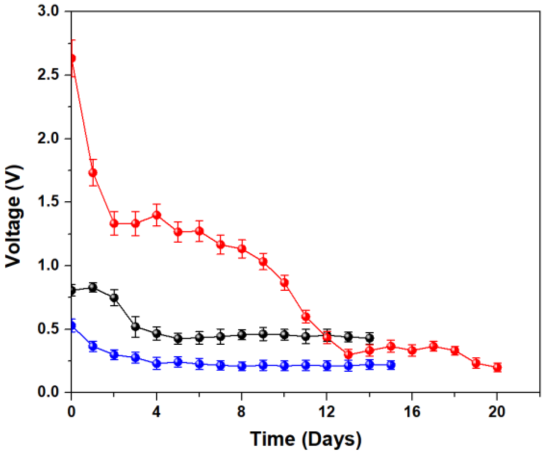

Figure 9: Measurement of Zn-Cu bio-battery capacity with ambarella peel concentration ratio.

There exist numerous limitations to this research. The peel of the ambarella fruit may have a lower concentration of ions compared to lemon juice, resulting in a decrease in the flow of ions and, as a result, a reduction in the formation of electrical current. The acidity of lemon juice, indicated by its lower pH, can intensify the electrochemical reaction and augment the current output. The pH of the ambarella peel may be higher, which could lead to a decrease in the efficiency of electron transmission. Lemon juice has a higher concentration of citric acid, which functions as a potent electrolyte. The peel of the Ambarella fruit may not contain sufficient levels of powerful acids or other active electrolytes that are essential for effective charge transfer. The presence of lignin, cellulose, and hemicellulose in the ambarella peel electrolyte may result in higher internal resistance in this biobattery, hence lowering the total current output. The efficacy of the interaction between the electrodes and the ambarella peel may be less than that with lemon juice, either due to disparities in ion accessibility or surface responses.

Several enhancement measures can be implemented to optimize the performance and efficiency of the ambarella peel waste biobattery. By introducing citric acid or other organic acids into the electrolyte derived from ambarella peel, it is possible to enhance its acidity and enhance the movement of ions, hence potentially increasing the current production [34]. The addition of salts such as NaCl or KCl can improve the conductivity of the electrolyte by increasing the abundance of free ions that are available for the electrochemical reaction [35]. Utilize electrodes with greater surface areas, such as carbon-based materials, to enhance the number of sites available for electron transport in the reaction [36]. Applying catalysts or conductive compounds to the electrodes can enhance their interaction with the electrolyte [37]. One possibility is to mix ambarella peel with other natural electrolytes, such as lemon juice, to form a hybrid solution [38]. This combination could take advantage of the positive qualities of both materials, potentially increasing general electrical production.

The pH and H_2 measurements were conducted to ascertain the pH level, which indicates the concentration of H^+ in the solution and is correlated with the amount of dissolved H_2 resulting from the reduction reaction at the cathode.

Figure 10(a) demonstrates a consistent and upward trend. The rise in pH in the solution is a result of the diminishing concentration of H^+ ions, which occurs owing to the decrease in ionized galacturonic acid over time, caused by the reduction reaction to H_2. The concentration of hydrogen ions H^+ is directly linked to the concentration of dissolved H_2 due to a reduction reaction occurring at the cathode. The trend graph in Figure 10b represents the quantity of H_2 that can be quantified, which corresponds to the amount of H_2 that is dissolved.

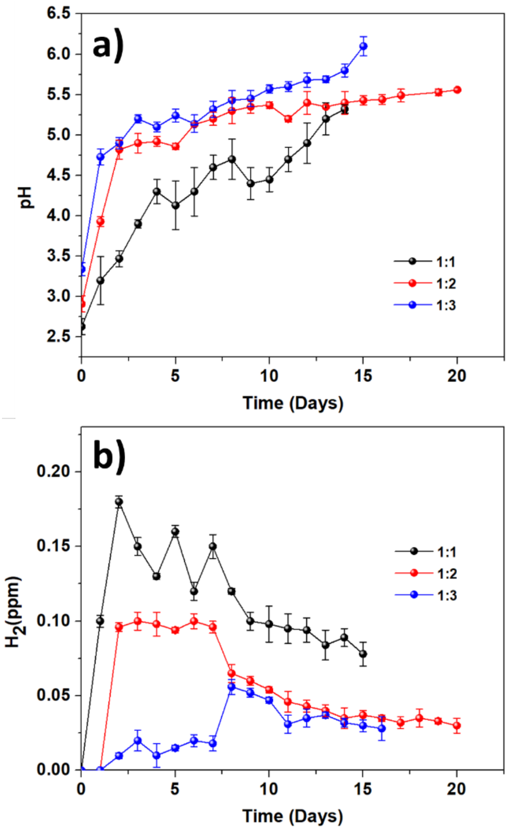

Figure 10: a) pH graph of ambarella peel electrolytes b) graph of dissolved H_2 in ambarella peel electrolytes.

The pH level of the electrolyte in a biobattery has a substantial impact on the efficiency and performance of the battery. A decrease in pH, indicating a higher acidity level, generally improves the electrochemical reactions at the electrodes by increasing the presence of H^+ ion, which aid in the transport of electrons. This enhanced ion flow has the potential to result in increased current production and improved overall battery efficiency. Nevertheless, when the electrolyte contains substantial amounts of lignin, cellulose, and hemicellulose, which are frequently found in plant-derived substances, the performance of the biobattery may be adversely impacted, even if the pH is low. The presence of intricate organic compounds might impede the movement of ions and elevate internal resistance, diminishing the efficiency of electrochemical reactions and subsequently, the overall performance of the battery. In addition, the H^+ ions in the electrolyte undergo a conversion to H_2 gas at the cathode during operation, resulting in a gradual rise in pH. The increase in pH can have additional effects on battery efficiency by modifying the conductivity and reaction kinetics of the electrolyte. Hence, in order to attain maximum efficiency in biobattery performance, it is crucial to take into account not only the optimization of pH, but also the electrolyte composition and the fluctuating pH levels during operation.

3.3.2 Maximum power density

The highest power density was measured to establish the correlation between electrochemical potential and battery output power. The investigation was performed utilizing a whole cell device circuit with an external resistance acting as a barrier. Incremental external resistance ranging from 10 MΩ to 1 Ω was introduced until a total of 7 data points were acquired. The voltage value at each site was utilized to determine the current and power density figures. The maximum power density is determined by the correlation between current and power density. According to the data in Figure 11, it was determined that the concentration ratio of 1:2 resulted in the highest maximum power density of 16.13 mW/m^2. This was followed by the concentration ratios of 1:1 and 1:3, which had maximum power densities of 12.6 mW/m^2 and 4.8 mW/m^2, respectively. The use of a 10Ω resistor resulted in the generation of three peaks of maximum power density. These findings align with the k_s value obtained from the analysis of the electron transfer rate constant. The concentration ratio of 1:2 resulted in the highest electron transfer rate, followed by the concentration ratio of 1:1, and finally, the concentration ratio of 1:3, which had the lowest electron transfer rate.

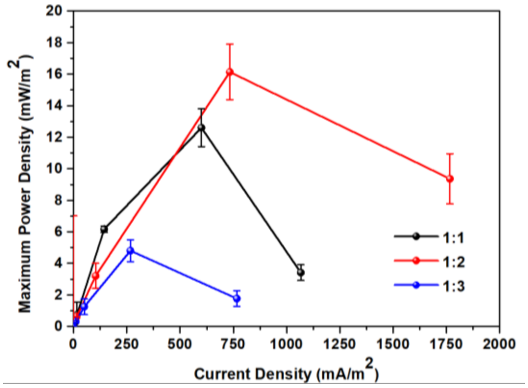

Figure 11: Maximum power density curves of ambarella peel electrolytes.

3.4 *Reaction mechanism of the Zn-Cu bio-battery using ambarella peel*

The reaction mechanism of a bio-battery with ambarella peel waste electrolyte is essentially similar to that of Zn-Cu batteries in general, with the exception of the electrolyte solution employed. Typically, Zn-Cu batteries utilize sulfuric acid as the electrolyte solution. However, this work explores the use of an electrolyte solution derived from ambarella peel, which contains galacturonic acid, in a Zn-Cu bio-battery. The presence of galacturonic acid in the electrolyte solution will result in the ionization of galacturonic ions and hydrogen ions. The subsequent text outlines the reaction mechanism occurring in Zn-Cu bio-battery cells utilizing ambarella peel electrolyte. Initially, galacturonic acid undergoes ionization, resulting in the formation of hydrogen ions and galacturonic ions. Subsequently, Zn^{2+} ions undergo a chemical reaction with ions present in the electrolyte. Ultimately, at the cathode, two hydrogen ions (H^+) undergo reduction to form hydrogen gas (H_2). Electrons move in a direction from the anode (Zn) to the cathode (Cu), while the direction of electric current flow is opposite. Electrons are conducted from the battery's negative terminal through the wire, and subsequently return to the battery's positive terminal, as shown in Figure 12.

$$2C_6H_{10}O_7 \longrightarrow 2C_6H_9O_7^- + 2H^+$$
$$Zn \longrightarrow Zn^{2+} + 2e^-$$
$$Zn^{2+} + [\,2C_6H_9O_7^- + 2H^+\,] \longrightarrow Zn(C_6H_9O_7)_2 + 2H^+$$
$$2H^+ + 2e^- \longrightarrow H_2$$

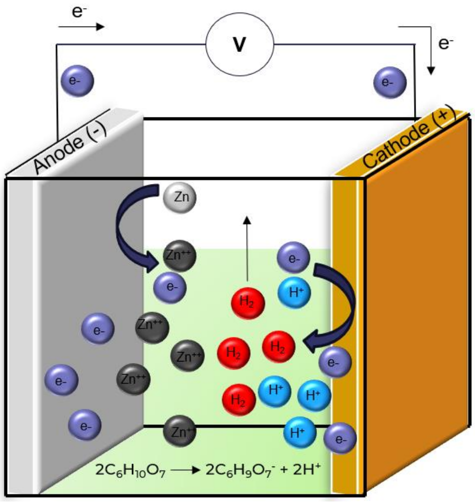

Figure 12: Illustration of reaction that occurred in the anode and electrode of biobattery.

3.5 *Degree of ionization*

The degree of ionization is a measure of the proportion of compounds that are ionized in a solution compared to the total number of compounds in the solution [39]. This study utilizes the degree of ionization to quantify the extent of ionization caused by galacturonic acid in electrolyte solutions employing ambarella peel. Galacturonic acid undergoes ionization, resulting in the formation of galacturonic ions and anions (H^+). The concentration of H^+ ions can be determined by measuring the pH of the solution. This measurement is then used to evaluate the extent of ionization of the electrolyte solution derived from ambarella peel.

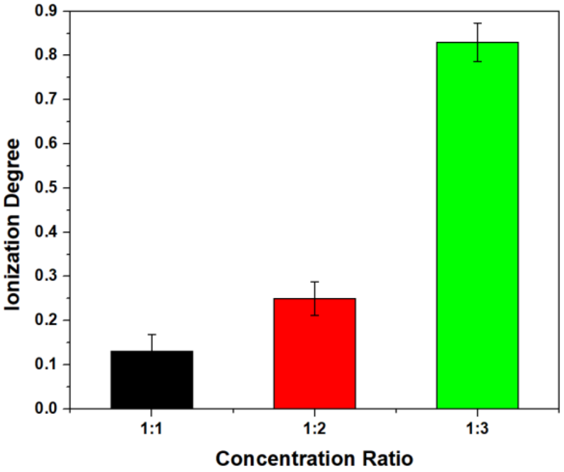

Figure 13: Degree of ionization at concentration ratios of 1:1, 1:2, and 1:3 of ambarella peel electrolyte solution.

The degree of ionization was calculated at different concentration ratios. At a 1:1 concentration ratio, the degree of ionization was found to be 0.13. At a 1:2 concentration ratio, the degree of ionization was 0.25. Finally, at a 1:3 concentration ratio, the degree of ionization was 0.83, as shown in Figure 13. By analyzing the degree of ionization, it becomes evident that the highest degree of ionization is observed in solutions with the lowest concentration ratio. This is due to the fact that in a more diluted solution, the equilibrium tends to favor the ionization of products. Conversely, in a more concentrated solution, the equilibrium shifts towards the presence of reactants [40]. The solution with the lowest concentration ratio exhibits the highest level of ionization. However, in terms of absolute values, the concentration of hydrogen ions (H^+) produced is not greater than that of the solution with a lower degree of ionization. The degree of ionization is influenced not only by the concentration of hydrogen ions produced, but also by the initial concentration of undissociated acid. The degree of ionization (α), with a value between 0 and 1, suggests that the solution is a weak electrolyte solution. Therefore, it can be concluded that the organic acids present in the ambarella peel are weak acids.

4 Conclusions

The electrochemical analysis of bio-batteries utilizing ambarella peel as the electrolyte material revealed significant findings. Ambarella peel, a fruit waste with acidic properties from its organic acids such as uronic acid, titrated acid, and ascorbic acid, was tested to evaluate its potential as a raw material for bio-battery electrolytes. The half-cell analysis using cyclic voltammetry electrochemical analysis revealed the presence of an oxidation peak at a potential of 0.5 V vs Ag/AgCl, indicating the conversion of uronic acid to aldaric acid. Additionally, two reduction peaks were observed: the reduction of hydrogen ions to H_2 at 0 V vs Ag/AgCl, and the reduction of H_2O at –0.42 V vs Ag/AgCl. The investigation of the rate determining step indicated that the reduction-oxidation reaction occurring in the electrolyte solution with ambarella peel was a surface reaction. In the analysis of the electron transfer rate constant (k_s), the biggest value of k_s was seen at a ratio of 1:2, specifically 0.722 ± 0.05 s^{-1}. This value was compared to the k_s values at concentration ratios of 1:1 and 1:3, which were 1.231 ± 0.07 s^{-1} and 0.474 ± 0.005 s^{-1}, respectively. Based on battery capacity tests, the study of the whole cell revealed that a concentration ratio of 1:2 resulted in the highest battery capacity of 0.0816 mAh. The battery capacity for a concentration ratio of 1:1 was 0.0048 mAh, and for a concentration ratio of 1:3, it was 0.00432 mA.h. The maximum power density analysis, using a concentration ratio of 1:2, yielded the highest maximum power density of 16.13 mW/m^2. This was followed by concentration ratios of 1:1 and 1:3, which had maximum power densities of 12.6 mW/m^2 and 4.8 mW/m^2, respectively. These results are comparable to the measurements of battery capacity. Furthermore, the analysis of the ionization degree of the electrolyte solution derived from ambarella peel waste reveals that it is a solution with low electrolytic conductivity. The electrochemical properties of bio-batteries utilizing ambarella peel waste electrolytes were analyzed in both whole cell and half-cell configurations. The optimal concentration ratio for these batteries was found to be 1:2, outperforming concentration ratios of 1:1 and 1:3. This study emphasizes the considerable potential of utilizing ambarella peel waste as an electrolyte substance for bio-batteries, emphasizing its cost-efficiency and environmental advantages. The findings indicate a promising direction for future progress, with the potential to enhance the battery business by providing a sustainable and economically feasible substitute for traditional electrolytes. These developments have the potential to create environmentally friendly energy storage solutions and contribute to a more sustainable future.

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Author Contributions

M.C.: conceptualization, investigation, methodology, research design, data analysis, writing, reviewing, funding acquisition, and editing; R.A.P.P.: conceptualization, investigation, data collection, analysis, writing, reviewing, and editing; N.N.: conceptualization, data analysis, writing, reviewing, and editing, project administration. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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