The effect of lime (Citrus aurantifolia Swingle) electrolyte filtrate addition on conductivity and electricity of hydrogel aluminium battery based on carboxymethyl cellulose

E Sundari¹, M H S Ginting*, A H Rajagukguk¹, E Misran¹, Iriany¹, K A Hasibuan¹ and M Lubis¹

¹ Department of Chemical Engineering, Faculty of Engineering, Universitas Sumatera Utara, Medan, North Sumatra 20155, Indonesia

*E-mail: hendra.ginting@usu.ac.id

Abstract. Hydrogel Aluminum Battery is a promising source of electrical energy using electrolytes polymer hydrogel. This research aims to determine the effect lime electrolyte addition on ionic conductivity and electrical characteristic values of hydrogel aluminium battery produced. The method used for making hydrogel is gelatinization method. Based on this research, the best conductivity value obtained is $3.968 \times 10^{-3}$ S/cm from the combination of CMC 2% on the addition of 100 ml. The highest voltage obtained from hydrogel aluminium battery is 1.6129 from the combination of CMC 2% on the addition of 100 ml electrolyte. The highest DC current is 14.077 mA from the combination of CMC 2% on the addition of 100 ml and the highest battery power obtained is 22,805 mW from the combination of CMC 2% variation at the addition of 100 ml electrolytes.

1. Introduction

Generally, electrolytes that used on liquid electrolytes (AlCl₃) have a high corrosion rate. Therefore, a study on an electrolyte form for batteries is needed. One of the options is a hydrogel, which is a Gel Polymer Electrolyte(GPE). GPE on a battery acts as an electrolyte and a separator on a battery for battery safety. Hydrogels are polymers that can absorb a certain amount of water without dissolving or losing the structural integrity of the polymer [1]. GPE can prevent leakage, increase its mechanical stability, and conductivity [2]. GPE can be considered as an alternative for battery production. GPE material that is often used is made from fossils material whose numbers are decreasing such as polyvinylidene fluoride (PVDF), and cannot be composed causing environmental pollution [3]. Hence, a study is needed on biocompatible and renewable materials such as cellulose.

Cellulose is a material that is easily obtained, has a large quantity in nature, has biocompatibility properties, is easily degradable, has good chemical stability, environmentally friendly, good mechanical properties, and thermostability that promises an alternative energy storage material on aluminum ion batteries [1]. CarboxymethylCellulose (CMC) is water-soluble anionic ether cellulose, produced by reacting cellulose alkali with monochloroacetic acid or sodium salt [4]. CMC is the best cellulose adhesive for anodes but it has poor electrical properties because it is an insulating material that can cause the conductivity to decrease. Thus, an additional conductive material is needed to increase the conductivity value in the form of electrolytes. Wang et al (2019) used AlCl₃ as its electrolyte but using chemical material can cause corrosion [5].
Therefore, in this study, organic material such as lime will be used. Lime (*Citrus aurantifolia Swingle*) has a citric acid content of 8% of the weight of fruit [6]. The aim of this study is to produce higher quality and ecologically friendly aluminum battery products, through conductivity and electrical test.

2. Materials and Method

2.1. Materials

Materials used in this experiment are aquadest (H₂O) as solvents, *CarboxymethylCellulose* (CMC) as a matrix in hydrogel formation, activated carbon as a filler in the battery, *polyvinyl alcohol* (PVA) as a binder slurry active, lime filtrate as electrolytes, glycerol 98% as the plasticizer, and graphite as an active material for anodes and cathode in the manufacture of batteries.

2.2. Electrolyte preparation

Fresh lime is cut into two halves and separated from the seeds. Lime is squeezed and filtered with filter paper. Lime filtrates are taken. A glass container is prepared that has been sterilized. The lime filtrate is put into the container. The container is sealed to avoid contamination from microbes.

2.3. Cathode making

Dissolved 1 gram PVA in aquadest while heated to a hotplate with a temperature of 100°C. Leave the solution for 1 hour until it is homogeneous and forms a hydrogel [7]. A total of 1 gram of graphite little by little into the solution. Then add 0.1 gram of activated carbon to the mixture while mixing it until it is homogeneous. The homogenous mixture then is taken to do coating in anode manufacture on aluminum foil surface and copper foil surface as the cathode on the battery. The coated aluminum and copper foil the dried on a hotplate with a temperature of 150°C [7].

2.4. Hydrogel production

A total of 100 ml of aquadest is heated in a beaker using a hotplate. CMC with variation of 2%, 3% and 4% (w/v) of aquadest weighed. Lime filtrate with a ratio of 0.5:1; 0.75:1, and 1:1 (v/v) is prepared. A total of 15 ml of glycerol is prepared as the plasticizer. Then, CMC is added to the aquadest while stirring it with a magnetic stirrer for each variation. Leave it until a homogeneous solution formed. The lime electrolyte is added for each variation. Plasticizer is added to the solution. Then, the solution is stirred until the temperature reaches 60°C [8]. Stirring is stopped when it has reached the desired temperature and make sure the solution is homogeneous. The beaker glass containing the solution is then cooled before printing and the pH of the solution is measured. Then poured the solution into a petri dish and then dried in the oven at 80°C for 4 hours. The petri dish is removed from oven and chilled in a desiccator for 3 hours [8]. The hydrogel removed from the petri dish to analyze the ionic conductivity.

2.5. Battery packaging with the sandwich method

The battery packed in a sandwich sequence of anode-hydrogel-cathode-anode. Then, the battery is put inside a 4x5 cm package. Next, the container is sealed using sealer [8].

2.6. Battery characterization

2.6.1. Conductivity test

Hydrogel conductivity testing using ohmic heating cell and electrical testing using multimeter and AC power supply. This method applies ohm’s law to get the value of resistance. The data generated consists of voltage (V) and Current (I) from the hydrogel. The Equations used in the conductivity test is as follows [9]:

\[ R = \frac{V}{I} \]

\[ P = \frac{V^2}{R} \]

\[ P_{AC} = \frac{P_{DC}}{\cos^2 \phi} \]

Where:
- \( R \) is the resistance (ohm)
- \( V \) is the voltage (volts)
- \( I \) is the current (amperes)
- \( P \) is the power (watts)
- \( P_{AC} \) is the power in AC
- \( \phi \) is the phase angle
\[ R = \frac{V}{I} \]  \hspace{1cm} (1)
\[ \sigma = \frac{L}{RA} \]  \hspace{1cm} (2)

AC power supply that is used in this test is adjustable 0-220V/50-60Hz and current 0-4A. The type of multimeter in this test is the UNI T61E multimeter which has a frequency response specification at 45Hz-10kHz so that it can record current and voltage data on the battery.

2.6.2. Electricity test
The data obtained in the electrical test are voltage and current values using a multimeter type UNI T61E. Voltage and current testing are performed for batteries that have been fabricated. The multiplication between voltage and current will obtain the value of the power produced. Equations used in the power test [9]:

\[ P = IV \]  \hspace{1cm} (3)

3. Results and Discussion

3.1. Effect of lime electrolyte amount on hydrogel conductivity
The conductivity value increases as the number of electrical conductivity measurements carried out to assess the contribution of ionic movement in the hydrogel. The electrolytes used in this research lime filtrate. Lime has a weak acidic compound which is citric acid (C$_6$H$_8$O$_7$) of 7-8% [6]. Electrolytes or battery ionic conductors provide an ion transfer medium [10]. The ions conductivity in the polymer electrolytes is mainly affected by the number of moving ions and the movement of the ions [11]. The more moving ions are in CMC, the more conductivity produced as it is easier to transfer electrons from anode to cathode.

![Figure 1](image_url)

**Figure 1.** Effect of lime electrolyte amount on CMC 3% to ion conductivity

In Figure 1, it can be seen that the value conductivity increases with how much electrolytes added. The value of conductivity increases with the addition of lime electrolyte with volume variations of 50, 75, and 100 ml. Therefore, the best conductivity value in this study is by using CMC 3% with 100 ml of electrolytes and 15 ml of plasticizer glycerol with a value of 3.968x10$^{-3}$ S/cm. The lowest conductivity value in this study is on a CMC 4% with 50 ml electrolytes with a value of 4.705x10$^{-4}$ S/cm. The conductivity values decrease due to a rejoining of the salt ions to form neutral ions [12].
3.2. The effects of lime electrolyte amount on the battery electricity values

3.2.1. The effects of lime electrolyte amount on DC voltage of hydrogel aluminum battery
The batteries are made from lime electrolytes with the addition of a 15 ml plasticizer. The addition of electrolytes to polymer batteries affected by ionic mobility. The H\(^+\) ion that's present on lime electrolytes can move from one place to another, filling the space with an H\(^+\)ion [13]. So, the conductivity of hydrogel will increase with the movement of the ions [11].

![Figure 2](image-url)

**Figure 2.** Effect of lime electrolyte amount on CMC 2% to voltage

In Figure 2, it can be seen that the voltage value increased with the addition of electrolyte. The current values increases as lime electrolytes added with variations of 50, 75, and 100 ml. The highest voltage value is at CMC 2% variation with the addition of 100 ml electrolytes of 1.6129 volts. Too many ions can cause ion mobility to decrease because higher ion density can result in a drop in value [14]. The lowest voltage value is at CMC 4% variation with the addition of 75 ml electrolytes of 1.0337 volts.

3.2.2. The effects of lime electrolyte amounts on hydrogel aluminum battery current
The citric acid (C\(_6\)H\(_8\)O\(_7\)) contained in lime electrolytes can produce currents in a battery. An acid solution can transport electrons and produce an electric current [15]. This is because the H\(^+\) ion on electrolytes can be transferred from anode to cathode [13].

![Figure 3](image-url)

**Figure 3.** Effect of lime electrolyte amount on CMC 2% to Current
In Figure 3, it can be seen that the value of current increased with the addition of lime electrolytes. The addition of lime electrolytes with variations of 50, 75, and 100 ml and 15 ml of glycerol plasticizer increased the current value. This shows that the more electrolytes added, the more H\(^+\) ions dispersed inside the CMC. Thus, the highest current value obtained in this experiment by using the combination of CMC 2\% with the addition of 100 ml of lime electrolyte with a current value of 14.077 mA. The lowest current value in this experiment by using the combination of CMC 4\% with the addition of 50 ml electrolyte with a current value of 4.258 mA.

3.2.3. The effects of lime electrolytes on DC power of hydrogel aluminum battery
The power generated in the battery is tied to current and voltage generated. This is because the power generated is a multiplication of both the current and the voltage of the battery. The more powerful the current is, the more power the battery can produce. This shows that ion mobility in electrolytes is bigger because of the dispersion of ions in CMC [11]. This causes the power generated in the battery to increase.

![Figure 4. Effect of lime electrolyte amount on CMC 2\% to battery power](image)

In Figure 4, it is seen that the resulting power increases as the electrolyte increases. It shows that the H\(^+\) ion movement in citric acid from lime electrolytes dispersed at CMC and it fills up the blank space at CMC hydrogel. The highest power derived from this experiment is the combination of CMC 2\% in additions of 100 ml electrolyte with a value of 22.705 mW. Whereas the lowest value is the combination of CMC 4\% in addition of 75 ml electrolyte with a value of 6.309 mW.

4. Conclusion
The highest conductivity value in this study of the combination CMC 3\% in addition to 100 ml electrolyte is 3.968 \(x10^3\) S/cm and the highest voltage value of the combination CMC 2\% with the addition of 100 ml electrolyte is 1.6129 Volt. The highest current value of combination CMC 2\% with the addition of 100 ml electrolyte is 14.077 mA and the highest power of combination CMC 2\% with the addition of 100 ml electrolyte is 22.705 mW. High electrical results are obtained because of the mobility of ions in the electrolyte to the CMC network while the low conductivity and voltage values are obtained due to the formation of neutral ions that occur between the electrolyte and CMC.

References
[1] Hu X, Yongmei W, Liangliang Z and Man X 2020 Construction of self-assembled polyelectrolyte complex hydrogel based on oppositely charged polysaccharides for sustained delivery of green tea polyphenols, Food Chemistry. Elsevier, 306, p. 125632
[2] Bose P, Deb D and Bhattacharya S 2019 Lithium-polymer battery with ionic liquid tethered
nanoparticles incorporated P(VDF-HFP) nanocomposite gel polymer electrolyte, *Electrochimica Acta*. Elsevier Ltd, 319, pp. 753–765

[3] Zhu Y S, Xiao S Y, Li M X, Chang Z, Wang F X, Gao J and Wu Y P 2015 Natural macromolecule based carboxymethyl cellulose as a gel polymer electrolyte with adjustable porosity for lithium ion batteries Journal of Power Sources, 288, pp. 368–375.

[4] Casaburi A, Ursula M R, Patricia C, Analia V and Maria L F 2018 Carboxymethyl cellulose with tailored degree of substitution obtained from bacterial cellulose, *Food Hydrocolloids.*, 75, pp. 147–156

[5] Wang Y, Fangyu G and Kanghua C 2019 Graphene composite plastic film as current collector for aluminum-graphite batteries, Materials Letters. Elsevier B.V., 254, pp. 436–439

[6] Kristina L P, Stephen Y, Ross P H and Dean GA 2008 Quantitative Assessment of Citric Acid in Lemon Juice, Lime Juice, and Commercially-Available Fruit Juice Products , Journal of Endourology, 22(3), pp. 567–570

[7] Iim F and Endarko 2013 Electrode Fabrication and Characterization for Capacitive Systems Deionization (CSD) in The NaCl Solution Desalination Process Freezing-Thawing Method (Surabaya: Institute of Sepuluh Nopember), 01, p 137

[8] Han Q, Xiaowei C, Shuming Z, Yunzhao L, Biao Z, Jianhua Y and Yu L 2018 Durable, Flexible Self-Standing Hydrogel Electrolytes Enabling High-Safety Rechargeable Solid-State Zinc Metal Batteries, *Journal of Materials Chemistry A*. Royal Society of Chemistry, 6(45), pp. 23046–23054

[9] Samprovalaki, K., Bakalis, S. and Fryer, P. J. 2007 Ohmic heating: models and measurements, Heat Transfer in Food Processing, 13, pp. 159–186

[10] Linden D and Reddy TB 2002 *Introduction, Linden’s Handbook of Batteries.*

[11] Osman Z, Ibrahim Z A and Arof A K 2001 Conductivity enhancement due to ion dissociation in plasticized chitosan based polymer electrolytes, *Carbohydrate Polymers*, 44(2), pp. 167–173

[12] Kadir M F Z, Aspanut Z, Majid S R and Arof A K 2011 FTIR studies of plasticized poly(vinyl alcohol)-chitosan blend doped with NH4NO3 polymer electrolyte membrane *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy* 78(3), pp. 1068–1074

[13] Buraidah M H, Teo L P, Majid S R and Arof A K 2009 Ionic conductivity by correlated barrier hopping in NH4I doped chitosan solid electrolyte *Physica B: Condensed Matter*, 404(8–11), pp. 1373–1379

[14] Majid S R and Arof A K 2005 Proton-conducting polymer electrolyte films based on chitosan acetate complexed with NH4NO3 salt *Physica B: Condensed Matter*, 355(1–4), pp. 78–82

[15] Deby S and Nurmasiyitah 2019 Effect of Electrode Material on The Electricity of Oranges and Tomatoes as an Alternative Energy Solution vol 2 p 2