

"Water-In-Salt" Electrolyte For High Temperature Aluminum Ion Battery Application

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Abstract

This study examines aluminum chloride hexahydrate (AlCl_3) in the form of water-in-salt and 1M liquid as an electrolyte salt in an Aluminum Ion Battery. To demonstrate battery electrochemical performance, linear sweep voltammetry and cyclic voltammetry are conducted at room temperature and 50°C. Energy activation is examined by measuring its ionic conductivity at 30, 40, and 50°C. In addition, scanning electron microscopy and energy dispersive X-rays are used to examine the sample's morphology. During a cyclic voltammetry measurement, water-in-salt AlCl_3 demonstrates superior electrochemical performance. Besides, a water-in-salt AlCl_3 battery could offer good ionic conductivity of 0.013 S/cm at room temperature and 0.0064 S/cm at 50°C. Moreover, according to the SEM and EDS data, water-in-salt AlCl_3 may reduce electrode deterioration both in the anode and cathode. The capability to suppress the hydrogen evolution reaction is an important key to improving the aluminum ion battery performance.

Keywords: Ion Battery, Aluminum Ion Battery, Water-in-salt Electrolyte, AlCl_3 , Hydrogen

1. Introduction

Science and technology are still progressing quickly, particularly in energy. There is a race among scientists to develop an affordable, dependable, and green energy storage system with a battery as one of the energy storage devices. The Lithium Ion Battery is the predominant battery technology utilized in contemporary applications, with numerous limitations. One of the major drawbacks of the Lithium Ion Battery is its tendency to overheat, which can lead to safety hazards [1]. Additionally, these batteries have a limited lifespan and gradually lose their capacity to hold a charge over time. Aluminum is one of the strongest candidates for replacing lithium as the primary material for making batteries [2, 3].

In addition, aluminum's abundant availability and cost-effectiveness as a primary resource render the long-term production of Aluminum Ion Batteries economically viable. In addition, the Aluminum Ion Battery exhibits a significant density capacity owing to its ability to facilitate the transmission of three electrons simultaneously during a charge/discharge cycle [4]. The increased density capacity of this technology enables a greater capacity for energy storage compared to alternative battery tech-

nologies. Moreover, Aluminum Ion Batteries exhibit an extended operational lifespan and can endure greater charge and discharge cycles, rendering them a dependable and resilient choice for many applications.

Ionic liquids, such as $[\text{EMIm}]\text{Cl}-\text{AlCl}_3$, Py_13C_1 , and $\text{EMIC}-\text{AlCl}_3$, are commonly used as electrolytes in Aluminum Ion Battery systems. Nevertheless, it should be noted that the utilization of ionic liquids in aqueous system batteries is limited due to their high cost and susceptibility to ambient environmental conditions [5]. Furthermore, it is necessary to employ particular techniques to utilize them as electrolytes effectively. The potential of utilizing water-in-salt as a substitute for ionic liquid in Aluminum Ion Batteries has been identified as a promising solution to address the current challenge in the development of such batteries. The electrolyte known as water-in-salt AlCl_3 is characterized by its high salt concentration in the water solvent. This electrolyte employs $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ as the salt component, chosen for its advantageous attributes such as cost-effectiveness, safety, and remarkable performance [2]. The water-in-salt electrolyte exhibits a notable increase in ion transport efficiency and energy density due to its high ionic concentration. In addition, utilizing $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ as

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the electrolyte salt offers exceptional benefits owing to its widespread availability and economical nature, making it an attractive choice for efficiently manufacturing aluminum ion batteries on a large scale.

2. Experimental method

2.1. Water-in-salt AlCl_3 dan 1M AlCl_3 synthesis

The aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) product was purchased from Puduk Scientific, while distilled water was utilized as the main component of the electrolyte. The sample is referred to as "water-in-salt AlCl_3 " and "1 M AlCl_3 ." In order to synthesize water-in-salt AlCl_3 , a mixture of 32.8 gr of AlCl_3 and 1 kilogram of distilled water is prepared, forming a solid watery salt. On the other hand, preparing a 1 M AlCl_3 sample requires dissolving 2.45 grams of the salt in 1000 milliliters of distilled water. The water and salt undergo a mixing process at 60°C for 30 min. To prevent moisture and contaminants, a salt sample combination is placed in the airtight container prior to use.

2.2. Aluminum Ion Battery Assembly

The Aluminum Ion Battery comprises of an aluminum foil, a copper foil coated with a graphite slurry, and filter paper as anode, cathode, and separator, respectively. The cathode is prepared by mixing graphite, super P, and CMC binder with a 9:8:2 weight ratio [6]. The mixture is ground with solvent to provide a slurry-like mass of 2 grams. The slurry was then coated into the copper foil and dried at 70°C for 24 hours. After the drying process, the cathode is placed in the dry area before use. Based on Figure 1, a 4x4 cm battery is assembled by sandwiching the anode, filter paper or water-in-salt mixture, and cathode. The 1M AlCl_3 batteries system will use a filter paper separator. However, because water-in-salt AlCl_3 serves as an electrolyte and a separator, an additional separator is not necessary.

2.3. Characterization of Aluminum Ion Battery

A potentiostat measurement is used in the testing of aluminum ion batteries. This measurement provides infor-

mation on the oxidation-reduction process and the resistance of the tested battery through linear sweep voltammetry (LSV), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) tests. The potential window will display the range of battery current and voltage. Moreover, the EIS test can calculate the ion conductivity and activation energy. Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDS) Spectroscopy are used to evaluate the surface morphology and the elements of the anode and cathode of an Aluminum Ion Battery.

3. Results and Discussion

3.1. Linear sweep voltammetry

Linear sweep voltammetry was conducted to determine the electrochemical performance of electrolytes, including the reduction process and a hydrogen evolution reaction (HER). The electrolyte is injected into a half-cell setting using aluminum foil and stainless steel as electrodes. A Half-cell system was completed for an electrochemical electrolyte test with a 0.4 V to -3 V potential range to assess the presence of a hydrogen evolution process.

According to Figure 2, the water-in-salt reduction process is more stable than the 1 M AlCl_3 electrolyte system. The graph demonstrates that the hydrogen evolution process on the water-in-salt AlCl_3 occurs smaller than 1 M AlCl_3 . The appearing peaks on the graph can be represented as the reduction of electrolyte and hydrogen evolution process for the first and second peaks, respectively, on the range between -0.6 V and -1.0 V. Basically, an aqueous environment is used to facilitate the hydrogen evolution process. As observed in Figure 3, the water-in-salt AlCl_3 electrolyte possesses a steady reduction process than the 1M AlCl_3 electrolyte [7, 8]. In the potential range of -0.6 V to -1.7 V, 1M AlCl_3 undergoes a vast and unstable reduction process. This reaction may be caused by hydrogen generation during the hydrogen evolution reaction process, which occurs at a potential less than 0 V. The test involves the formation of bubbles due to the hydrogen evolution process in 1M AlCl_3 electrolyte.

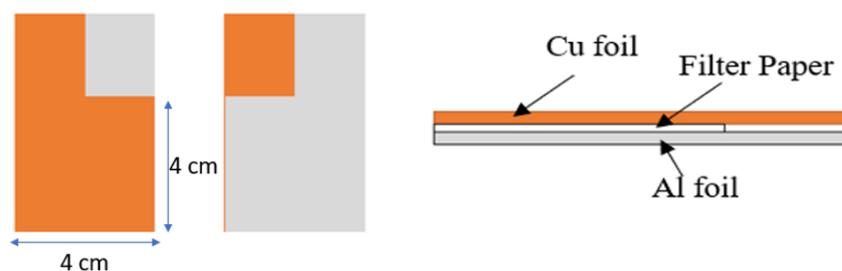


Figure 1. Aluminum Ion Battery Schematic Diagram

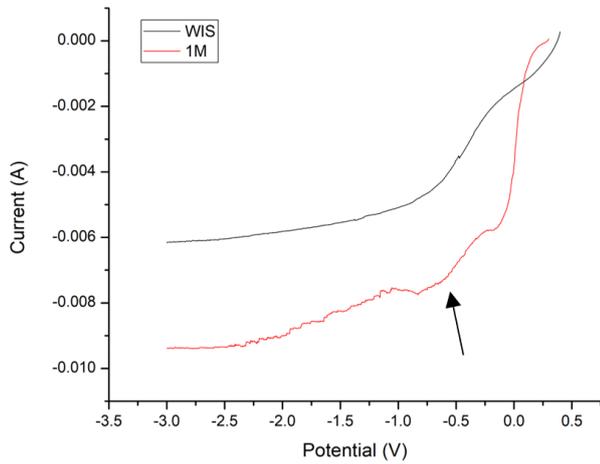


Figure 2. Reduction curve of water-in-salt AlCl_3 and 1M AlCl_3

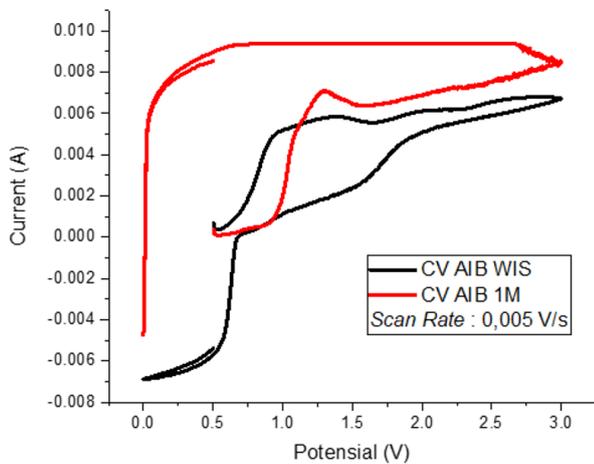
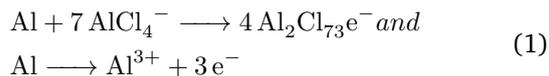


Figure 3. Graph of Cyclic Voltammetry of water-in-salt AlCl_3 and 1M AlCl_3

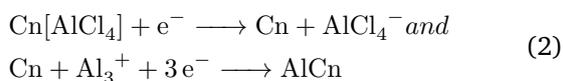
3.2. Cyclic Voltammetry at Room Temperature

Autolab 87662 is used to perform the cyclic voltammetry. The purpose of cyclic voltammetry is to emphasize the electrolyte's reduction and oxidation processes [9]. The first battery test was conducted at room temperature (25°C) with a scan rate of 0.005 V/s , an initial potential of 0.5 V , and a 0 V to 3 V potential range. In the discharging process, an oxidation reaction occurs at the anode and a reduction reaction at the cathode.

Anode:



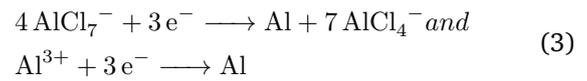
Cathode:



In contrast, in the charging, a reduction and oxida-

tion reaction occurs at the anode-cathode, respectively.

Anode:



Cathode:

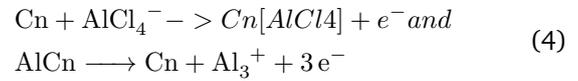


Figure 4. Trace of water appear on the 1 M AlCl_3 sample

The reaction in the charging–discharging process shows that the AlCl_4^- always undergoes intercalation and deintercalation at the cathode [2].

Figure 3 shows that AlCl_3 conducts a steady oxidation-reduction process, as shown in the equations 1,2,3,4. The interaction between the electrode and water-in-salt electrolyte AlCl_3 is stable due to the intercalation and deintercalation of 7AlCl_4^- at the cathode during charging and discharging. During oxidation processes between 1.5 V and 3.0 V , the reduction reactions occur between 1.85 V and 0.8 V . Water stability in salt Aluminum Ion Battery is due to the equilibrium of ions entering and exiting the cathode. It can be observed from the graph that the Aluminum Ion Battery with water-in-salt AlCl_3 conducted a reduction process between 0.6 V and 0 V . The reduction process is decreased by using a water-in-salt electrolyte with a wider potential window than 1M AlCl_3 electrolyte. This reduction may correlate with the hydrogen production during the process. Figure 4 shows the appearance of water droplets due to the hydrogen evolution reaction resulting from reaction 5 [10].



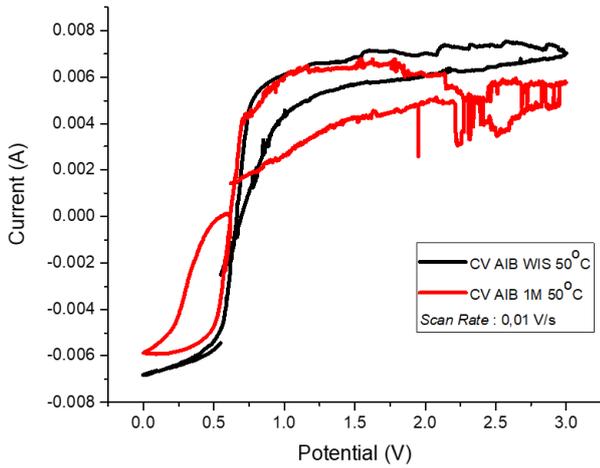


Figure 5. Graph of Cyclic Voltammetry of water-in-salt AlCl_3 and 1M AlCl_3 at elevated temperature

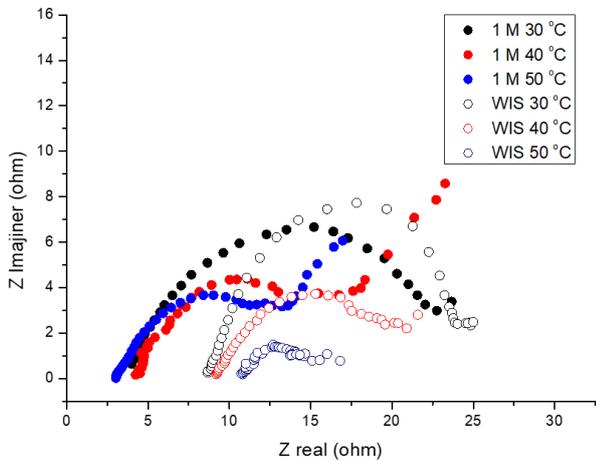


Figure 6. Electrochemical Impedance Spectroscopy (EIS) result for 1M AlCl_3 and water-in-salt (WIS) AlCl_3 at temperature 30, 40, and 50°C

Table 1. Ionic Conductivity Calculation

Sample	R (Ω)			σ (S/cm)		
	30°C	40°C	50°C	30°C	40°C	50°C
Water-In-Salt AlCl_3	15.42	12.78	3.11	0.013	0.016	0.064
1M AlCl_3 1M	20.74	12.94	12.12	0.010	0.015	0.016

3.3. Cyclic Voltammetry at 50°C

To study the effect of high temperature, the cyclic voltammetry was carried out at 50°C using a scan rate of 0.01 V/s , a starting potential of 0.5 V , and a 0 V to 3 V potentials range. Figure 5 shows an oxidation-reduction process in cycles of testing the Aluminum Ion Battery at 50°C . In the Aluminum Ion Battery with 1M AlCl_3 electrolyte, the oxidation-reduction process is clearly shown in the cyclic voltammetry, which fluctuates as a result of the fast-moving ions in the electrolyte under the effect of the liquid phase and temperature. In addition, the

unstable CV graph on the Aluminum Ion Battery with 1M AlCl_3 was caused by water droplets obstructing the ions' movement during the test. The oxidation-reduction process in the Aluminum Ion Battery with water-in-salt AlCl_3 electrolyte seems smoother and more stable. The stability of the water-in-salt AlCl_3 at a high temperature is due to the capability of the water-in-salt to hold the heat compared to the liquid [11]. The cell is disassembled after high-temperature testing. The 1M AlCl_3 electrode shows a severe decay due to the rising water droplet during the hydrogen evolution reaction. Based on the cyclic voltammetry at room and high (50°C) temperature of water-in-salt AlCl_3 , the hydrogen evolution reaction is lesser than in the 1M sample, indicating the capability of water-in-salt to inhibit the hydrogen evolution reaction. The evolution of hydrogen can lead to hydrogen absorption into the aluminum, potentially causing hydrogen embrittlement that causes the aluminum electrode to be prone and cracking.

3.4. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) was used to measure the ionic conductivity by Nyquist graph where the x-axis is the real (Z') and the y-axis is the imaginary impedance (Z'') [12]. The EIS result in Figure 6 provides a comprehensive overview of the samples' behavior under elevated temperature conditions. This data allows for a thorough analysis of the samples' electrical properties and can provide valuable insights into their performance in high-temperature environments. Figure 6 shows that increasing temperature may decrease the resistance of the sample. The ionic conductivity value for all electrolyte types is increased linearly with increasing temperature. This increase in ionic conductivity with temperature can be attributed to the higher mobility of ions at elevated temperatures. The temperature rise provides more energy to the ions, allowing them to move more freely and, therefore, enhancing the overall conductivity of the electrolyte [12]. The calculation of total resistance and ionic conductivity is provided in the table below.

Based on Table 1, the Aluminum Ion Battery with 1M AlCl_3 exhibits a higher resistance value than water-in-salt AlCl_3 electrolyte. The liquid phase allows for faster diffusion of ions, resulting in improved ion transport compared to semi-solid-state electrolytes [13]. Additionally, the presence of free-moving ions enhances conductivity. Water-in-salt AlCl_3 is synthesized with a high concentration of salt on the electrolyte. This higher salt concentration in the water-in-salt AlCl_3 electrolyte leads to a greater number of free ions available for conductivity. As a result, the water-in-salt AlCl_3 electrolyte exhibits lower resistance and higher ion transport compared to the Aluminum Ion Battery with 1M AlCl_3 .

Table 2. Activation Energy Calculation

Sample	Slope	E_a (J/mol)
Water-In-Salt AlCl_3	-0.8006	6.65
1M AlCl_3	-0.2685	2.22

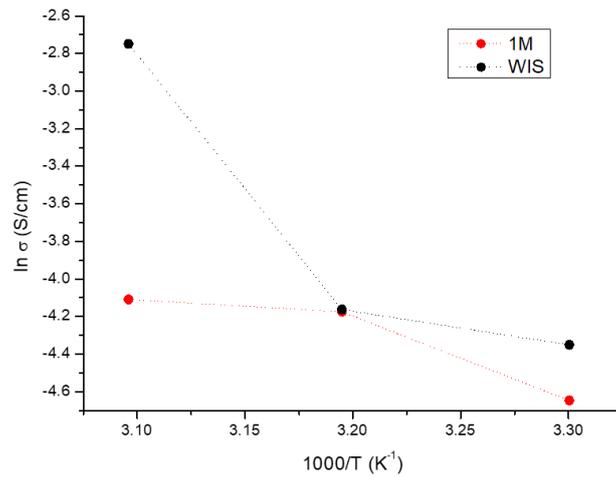


Figure 7. Arrhenius plot of 1M AlCl₃ and water-in-salt AlCl₃

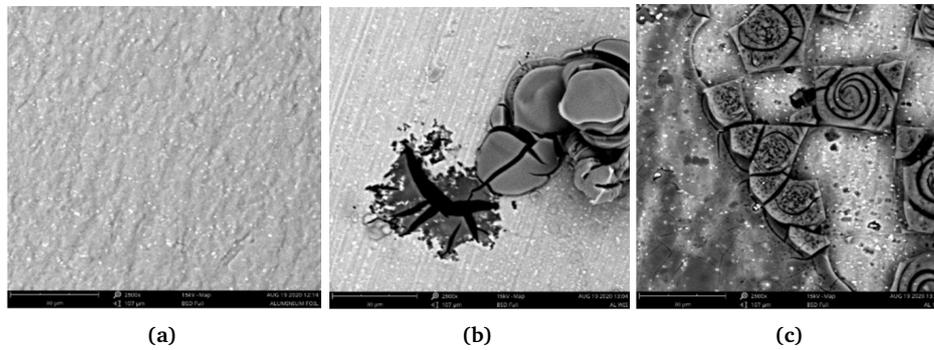


Figure 8. SEM results (a) aluminum foil before use on AIB, (b) aluminum foil on AIB water-in-salt AlCl₃ after 3 cycles of CV testing (c) aluminum foil on AIB 1M AlCl₃ after 3 cycles of CV testing

After the ionic conductivity values are evaluated, the activation energy can be determined. Activation energy is the minimum energy required for a chemical reaction [8]. Figure 7 shows the Arrhenius plot of both samples. The slope of the line is determined by linear fitting to predict the activation energy using equation 6.

$$\text{Slope} = -\frac{E_a}{R} \quad (6)$$

Where:

E_a : Activation energy, J/mol

R : Gas constant, J/K.mol

The activation energy value of the water-in-salt AlCl₃ electrolyte is higher than 1M AlCl₃, as shown in Table 2. The correlation between activation energy and the reaction rate is inversely proportional [14]. The reaction rate of the 1M AlCl₃ electrolyte was faster than the water-in-salt AlCl₃, which indicates that the kinetic reaction of the 1M AlCl₃ electrolyte was more rapid than the water-in-salt. On the other hand, water-in-salt AlCl₃ may slow the kinetic reaction and decrease the hydrogen evolution. This result is in good agreement with the CV result that water-in-salt suppresses the hydrogen evolution reaction.

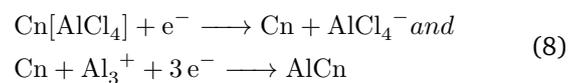
3.5. Morphology

The anode and cathode morphology of the Aluminum Ion Battery was conducted using Scanning Electron Microscopy (SEM). Thus, to determine the elemental content in the anode and cathode of the Aluminum Ion Battery using Energy Dispersive X-ray spectroscopy (EDS) scan point testing. The aluminum foil and composite graphite were used as an anode and cathode material in the Aluminum Ion Battery. The SEM image shows the anode morphology with water-in-salt AlCl₃ and 1M AlCl₃ after three cycles of the CV test on a complete discharge condition with the following chemical equations:

Anode:



Cathode:



The SEM results shown are 2500 times magnification.

Figure 8(a) shows the pristine aluminum foil of AIB. No defects were found on the anode surface. After undergoing three CV testing cycles, the morphology of aluminum foil on AIB water-in-salt AlCl_3 and AIB 1M AlCl_3 emerged the defects, with the most severe defects shown in AIB with 1M AlCl_3 (Figure 8(c)). The reaction of aluminum foil with the electrolyte used to create the defect resulted in aluminum dissolving into anions (AlCl_4^- and Al_2Cl_7^-) and cations (Al^{3+}) in water-in-salt AlCl_3 electrolyte and 1M AlCl_3 [15].

Tables 3 and 4 show the EDS of the aluminum foil electrode after three CV testing cycles. The aluminum content on the 1M AlCl_3 sample is lower than the water-in-salt AlCl_3 sample, and this result indicates the degradation of aluminum due to the hydrogen generative may dissolve the aluminum, as shown by the morphology image above. This degradation is likely caused by the reaction between the aluminum foil electrode and the hydrogen generated

during the CV testing cycles. The lower aluminum content in the 1M AlCl_3 sample suggests that more aluminum has dissolved compared to the water-in-salt AlCl_3 sample.

Table 3. EDS of Aluminum foil electrode of Water-in-salt AlCl_3

Element Number	Element Symbol	Element Name	Atomic Conc.
13	Al	Aluminium	39.86
8	O	Oxygen	56.59
6	C	Carbon	2.60
7	N	Nitrogen	0.95

Table 4. EDS of Aluminum foil electrode of 1M AlCl_3

Element Number	Element Symbol	Element Name	Atomic Conc.
13	Al	Aluminium	35.27
8	O	Oxygen	57.04
6	C	Carbon	6.09
7	N	Nitrogen	1.6

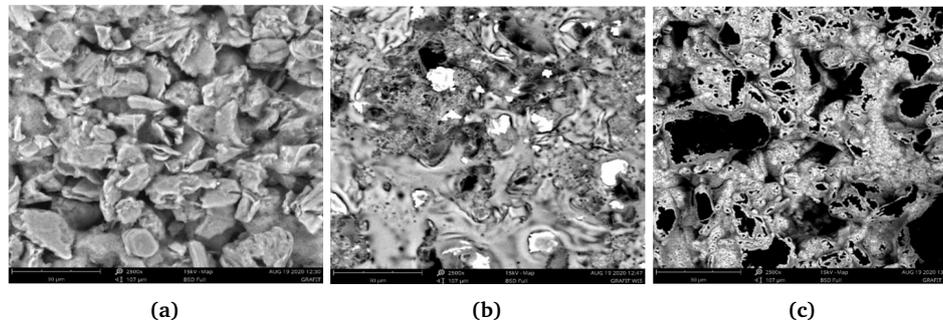


Figure 9. SEM results (a) composite graphite before use on AIB (b) composite graphite on AIB water-in-salt AlCl_3 after 3 cycles of CV testing (c) composite graphite on AIB 1M AlCl_3 after 3 cycles of CV testing

Table 5. EDS of Graphite electrode on the WIS

Element Number	Element Symbol	Element Name	Atomic Conc.
13	Al	Aluminium	35.27
8	O	Oxygen	57.04
6	C	Carbon	6.09
7	N	Nitrogen	1.6

Table 6. EDS of Graphite electrode on the 1M AlCl_3

Element Number	Element Symbol	Element Name	Atomic Conc.
8	O	Oxygen	12.79
6	C	Carbon	17.65
29	Cu	Copper	60.94
17	Cl	Chlorine	7.64
13	Al	Aluminium	0.54

Figure 9 shows the SEM result of graphite before and after the CV testing. Based on Figure 9, the water-in-salt AlCl_3 shows more compact than 1M AlCl_3 area. The hydrogen evolution during the cycling may deteriorate the graphite layer by hydrogenation toward water. This can be observed in the SEM images, where the graphite surface appears rougher and more damaged after CV testing compared to its initial state. The hydrogenation process caused

by the hydrogen evolution may lead to the degradation of the graphite layer, potentially affecting its performance in future cycles. Besides, the graphite decay on the battery is caused by the intercalation and deintercalation process, allowing the ion insert and deinsert on the graphite site to initiate the exfoliation damage over time.

Regarding the EDS testing in the table above, the carbon content of the AIB cathode with 1M AlCl_3 after three cycles of CV testing was significantly smaller than AIB water-in-salt AlCl_3 . The decreasing carbon content in the electrode is affected by the hydrogen, which may accelerate the cathode decay. Furthermore, the carbon is exfoliated, as shown in the SEM image. This demonstrates that water-in-salt AlCl_3 is superior to 1M AlCl_3 in Aluminum Ion Battery, especially at high temperatures. Al and Cl elements are produced from the AlCl_4^- intercalated on the graphite layer, which is distinguished by white dots on its morphology according to copper foil [2].

4. Conclusions

In conclusion, the water-in-salt AlCl_3 electrolyte solution proves better electrochemical stability than the 1M

AlCl_3 electrolyte solution. Based on cyclic voltammetry at high temperatures, the ability of water-in-salt to maintain heat provides better stability by minimizing the hydrogen generation that causes the decomposition of the aluminum and graphite electrodes. On the other hand, the ionic con-

ductivity result indicates that water-in-salt AlCl_3 exhibits greater ionic conductivity with higher activation energy, which may provide sufficient ionic conductivity and less reactive at high temperatures, thereby enhancing the safety of the battery.

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