Article

A Metal Accelerator Approach for Discharging Cylindrical Lithium-Ion Batteries in a Salt Solution

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Abstract: Recycling lithium-ion batteries provides sustainable raw materials. Crushing and separation are necessary for extracting metals, like lithium, from batteries. Crushing a battery carries a risk of fire or explosion. Fully discharging the battery is crucial for safe production. Discharging batteries in a salt solution is a simple and cost-effective large-scale process. However, it is important to note that there is a potential risk of corrosion and loss of battery elements when batteries are immersed in a salt solution. The purpose of this study is to investigate the effectiveness of two distinct methodologies at enhancing the voltage drop of a cylindrical battery when immersed in a salt solution while preventing corrosion. These techniques involve the application of iron and copper accelerators. A 20 wt.% salt water solution was chosen based on the research of several researchers. As the current flows through the metal parts, it encounters electrical resistance and forms an electric circuit with the electrolyte solution. This interaction converts electrical energy into various physical-electrical-electrochemical phenomena, leading to a decrease in battery voltage. Research revealed that the battery can be discharged up to 100% within 4 h without causing corrosion to its components. Another point to note is that if copper conductors are used, it is possible to decrease the battery voltage by around 90% within 8 h. The gap between the copper conductor and the battery had a direct impact on the battery’s discharge rate. Reducing the distance significantly increased the discharge rate, as confirmed by experimental evidence. This discharge mechanism was thoroughly described in a schematic, and, to further explain the electrochemical reaction, the Pourbaix diagram was utilized for both the Fe-Na-Cl and Cu-Na-Cl systems. Moreover, our theoretical predictions were validated through a chemical and mineralogical analysis of the precipitates that formed in the solution.

Keywords: NCA battery discharge; Fe flakes; copper conductor; voltage drop; electrolyte solution; residual voltage

1. Introduction

The power source for an electrical device is typically a battery, which is essentially a grouping of electrochemical cells. Lithium-ion batteries (LIBs) are in high demand due to the increasing popularity of electric mobility, including cell phones, laptops, power tools, and electric vehicles (EV). As of 2019, the global market saw a staggering 2.1 million electric vehicles sold, with projections indicating a remarkable increase to 60 million by 2040 [1,2]. Mobile appliances and EV growth drive LIB demand, causing material shortages for battery manufacturers. The cost of a battery, which directly impacts the price of electric devices and electric cars, is primarily determined by the price of cobalt and nickel, the active materials in the cathode [3–5]. Recycled materials sourced from urban waste offer
a cost-effective alternative to natural materials. Additionally, the mining industry is a massive integrated process, several times larger than the waste recycling industry, and it consistently presents challenges for environmental restoration [6,7]. The global battery recycling rate stands at around 50%, with Asia and Europe showing promising potential for higher recycling rates. China and Europe have reported recycling rates of about 80% [8,9]. Every year, researchers explore numerous methods and techniques for recycling LIBs, drawing on the fundamental principles of pyrometallurgy and hydrometallurgy. The pyrometallurgical technique has numerous benefits, such as achieving a metal recovery rate of over 95% through high-temperature processing. However, one disadvantage is its inability to extract lithium [10–13]. As a result, there has been a significant focus on researching the recovery of lithium from batteries in recent years. The initial stage involves extracting lithium using a hydrometallurgical approach. To achieve this goal, it is crucial to dismantle and recycle the battery, separating the components into metal, plastic, and carbon masses. When the battery is crushed or shredded, there is a high potential for fire or explosion. The reason for this is that if the anode and cathode of the battery are crushed and make contact, a residual charge causes a short circuit, leading to the creation of sparks. Simultaneously, the lithium in the battery reacts vigorously with the oxygen in the air, escalating the fire and resulting in an explosion [14,15]. Consequently, it is imperative to undergo a discharge or lithium stabilization process before breaking a battery. Effective methods for stabilization, such as electrical discharge, solution discharge, cryogenic pre-treatment, thermal pre-treatment, and in-process stabilization, have been identified [16,17]. Cryogenic pre-treatment, heat treatment, and crushing methods under inert gas have disadvantages, such as special equipment and high energy costs. According to Seoa et al. [18] and Hao et al. [19], submerging the battery in copper and graphite powder and creating a short circuit through the powder results in a significant discharge rate and a decrease in residual voltage to just over 0.5 V. However, there may be risks associated with overheating due to a potential short circuit, as well as the possibility of battery disintegration caused by internal heating during powder discharge [20]. Furthermore, discharging a substantial amount of batteries at once proves to be difficult. One proposed approach to discharging batteries in large quantities involves submerging them in an electrolyte solution. Figure 1 summarizes battery discharge methods and their advantages and disadvantages. The residual voltage of the battery enables an electrochemical reaction when discharging in a salt solution without external energy.

![Figure 1](image_url) **Figure 1.** Providing an overview of battery discharge methods’ features, advantages, and disadvantages.
Immersing a battery in water can cause a short circuit and discharge, while also releasing hydrogen and oxygen through electrolysis [21]. Electrolyte solutions enhance conductivity and the discharge rate, as proven by numerous studies. Based on extensive research and multiple conducted studies [22–28], it has been found that the most commonly observed approach to battery discharge involves the utilization of different types of brines and halides, among which NaCl brine has been identified as the most optimal choice. Jiefeng et al. [29], Lin et al. [30], James et al. [31], Zheng et al. [32], and Hassan et al. [33] compared the discharge of LIBs in various solutions, including NaCl, KCl, NaNO₃, Na₂CO₃, MnSO₄, NaOH, MgSO₄, and FeSO₄. The NaCl solution had the highest potency as an electrolyte, with a decreasing discharge rate as the salt content increased. The studies mentioned above highlighted the susceptibility of battery components to corrosion when exposed to a salt solution. In order to prevent corrosion, a study conducted by Mohammad et al. [34] examined the rate of discharge by submerging a copper wire, which was connected to a battery’s poles, into NaCl solutions with different concentrations. The discharge rate was found to be accelerated in a solution comprising 20 wt.% NaCl by weight, revealing an important finding. Severi et al. [35] conducted an experiment where they added zinc and iron powder to the bottom of a beaker filled with a 5 to 20 wt.% NaCl solution. In order to test the reaction, they set up corrosion-resistant platinum wires, connecting them to the battery poles and then placing them into the metal powder. The experiment concluded that the battery discharged the fastest in a 20 wt.% NaCl solution with iron powder, taking 4.4 h. Additionally, it should be noted that Hao et al. [19] successfully discharged their batteries by immersing them in flake graphite, while Nicole [36] achieved the same result using a salt solution with iron staples. Both studies highlighted that the battery components remained unaffected by corrosion throughout the process. However, the results of these tests revealed that effective discharge was only achieved after a duration of 24 h.

The main objective of this research was to find the most convenient, cost-effective, and innovative approach to discharging cylindrical LIBs using a salt solution. Our approach involved immersing the batteries directly in a NaCl salt solution while ensuring that no corrosion was induced. Based on the findings of Severi et al. [35] and Mohammad et al. [34], a 20 wt.% NaCl solution was determined to be the most appropriate. The tests were conducted using two approaches. (1) We submerged the battery in a salt solution containing an iron particle bed, and then discharged the battery by immersing it through the positive pole. Despite the fact that iron is capable of conducting electricity, it possesses a relatively high electrical resistance, which leads to the quick depletion of battery voltage due to the conversion of electrical energy into thermal energy. Moreover, iron is an economical and easily accessible material. (2) By immersing the discharging battery in the solution and introducing a copper conductor, it is possible to create a short circuit within the electrolyte medium. Copper was selected due to its high electrical conductivity, which is coupled with its relative abundance. Position the copper conductor slightly apart from the battery, creating a gap between them to avoid direct contact. The discharge rate was influenced by the gap size. In addition to providing a detailed explanation of the discharge process, we have prepared a schematic diagram and a Pourbaix diagram. These diagrams have been specifically designed to illustrate the thermodynamic stability areas and electrochemical reactions involved. Once the experiment was concluded, an extensive analysis was carried out on the precipitates that had formed in the solution. The results of this analysis served to validate our initial assumption of the electrochemical reactions occurring.

2. Materials and Methods

2.1. Experimental Materials
In this study, we utilized Samsung cylindrical-type lithium ion NCA batteries (3.78 V) as our experimental materials. The NCA battery had specific details: a reported nominal capacity of 3950 mAh, a minimum capacity of 2850 mAh, and a nominal voltage of 3.78 V. The package of a 32 V set was carefully opened and each battery was separated one by one. To discharge the batteries, they were fully submerged in salt water with a voltage of 3.78 V. The salt water was prepared using a popular sea salt brand called SAJO LLC, which is known for its purity and originates from South Korea. The sea salt is composed of 93 to 94.5% NaCl and various minerals such as MgCl, Na₂SO₄, MgSO₄, KCl, and CaSO₄. To prepare the salt water solution, 20 wt.% Sajo sea salt was introduced into 500 mL of distilled water. A thorough dissolution of the salt was achieved by diligently stirring the mixture. Using a digital pH-200 pH meter, the pH level of the salt water with a 20 wt.% concentration was measured to be 10.49. Table 1 provides information on the concentration and pH level of the salt water used during the discharge experiment.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Salt in Water, g per 500 mL</th>
<th>pH</th>
</tr>
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<tbody>
<tr>
<td>20 wt.%</td>
<td>10</td>
<td>10.49</td>
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2.2. Experimental Procedures

There were two approaches tested to enhance the rate of battery discharge in salt water, using iron parts and a copper strip as conductors. In Figure 2, the battery’s location during the discharge test is depicted, as well as the electrical circuit involving iron flakes and copper conductors. In the first test, iron powder and iron flakes with an irregular shape were placed at the bottom of a beaker containing the solution. Following that, a cylindrical battery was immersed in the iron particles, as illustrated in Figure 2a. As the electric current flowed through the metal parts, an electrochemical reaction occurred on the expansive surface of the iron particles, causing the battery voltage to rapidly decrease. When iron particles undergo electrochemical reactions, iron oxides and chlorides can be produced and deposited on their surface. In the next discharge experiment, a copper conductor was used and placed in two different positions at a specific distance from the battery poles, as depicted in Figure 2b,c. The copper conductor was placed at a specific distance and was isolated from the battery’s positive and negative poles. The specific gap between the battery’s poles and the end of the conductor in the electrolyte medium played a crucial role in determining the likelihood of an electrical short circuit. To measure the voltage drop, the discharge tests were conducted at intervals of 2, 4, and 6 mm, providing accurate data. The electrolyte solution (in Figure 2b) enabled the electric current to move from the positive to the negative pole, establishing an electrical circuit. Meanwhile, the copper conductor facilitated a short circuit by providing a shorter pathway for the current to flow through. Additionally, the copper conductor generated heat, leading to excessive energy consumption as it transferred that heat to the electrolyte. The difference in electrode potentials between the copper conductor and positive pole materials of the battery can lead to electrochemical reactions during discharge. From the salt water, hydrogen and chlorine ions were produced on the negative pole, creating their distinct gases. Furthermore, while the electrolytic cells were active, there was a risk of corrosion to the battery’s nickel-plated steel cap and aluminum valve. Figure 2c shows the placement of the battery, with the positive pole positioned at the end of the copper conductor, and the negative pole.
spaced 2, 4, and 6 mm from the opposite end. When the battery is set up like this, the copper strip acts as a pathway for the electrical current, resulting in a short circuit within the electrolyte solution, connecting the (-) pole of the battery and the strip’s end. The tests were conducted in a controlled environment at room temperature. Moreover, each discharge method underwent three rounds of testing, and the arithmetic mean of the battery voltage was used to report the findings.

Figure 2. Schematic diagram of electrochemical discharge using salt water with (a) iron particle bed; (b) no contact between copper conductor and battery; (c) copper conductor in contact with battery.

2.3. Analysis Methods

The battery voltages were measured using a UT201 clamp multimeter manufactured by UNI-T in Fangzhi city, China. To accurately measure low direct voltage (DC), we carefully inserted the red cable into the positive (+) input jack and the black cable into the COM negative (-) input jack of a multimeter. The positive pole of a battery underwent a red test, while the negative pole was tested with the black cable for 5 or 7 s. The voltage of the battery was measured every hour for the first 5 h, and then again after 5 h of discharging. Following the discharge experiment, the precipitate in the salt water underwent filtration using a vacuum pump and was subsequently dried at 100 °C for 24 h. This was carried out to prepare it for analysis using an X-ray fluorescence spectrometer (XRF) and X-ray diffraction (XRD) at the Collaborative Laboratory of Pukyong National University. The chemical composition of the precipitate and the products of the electrochemical discharge were analyzed using a Shimadzu XRF-1800 X-ray fluorescence spectrometer manufactured in Tokyo, Japan by Shimadzu Corporation. The sample was carefully placed inside a platinum crucible and inserted into an XRF machine. Inside the machine, a beam was directed into the sample holder, causing the sample to be ionized by X-rays in a vacuum environment. This XRD analysis was used to identify the compounds formed during the electrochemical discharge. For this analysis, the tool used was the X’Pert-MPD model manufactured in Malvern, UK by PANalytical, which was equipped with a 3 kW Cu-Kα X-ray tube. A scanning range of 10 to 80° was used for XRD data collection, which took 10 min and had a step size of 0.02°.

3. Results and Discussion

3.1. Discharge in Salt Water Using a Bed of Iron Particles

In order to effectively disperse the battery discharge in the salt solution, a specific quantity of metal was used to conduct the electric current. The iron has a standard electrode potential of $E^0 = -0.447$ V, allowing for the creation of an active electric cell in the electrolyte solution. A rapid depletion of battery voltage occurs in iron due to its high electrical resistance, resulting in the conversion of energy into heat. The research conducted by Severi et al. [35] supports the notion that the use of iron powder in batteries yields a greater discharge efficiency when compared to zinc powder ($E^0 = -0.76$ V). Additionally,
it should be highlighted that iron is both affordable and widely available. During discharge, various electrochemical and electrical processes occur simultaneously, such as water electrolysis, iron corrosion, iron chlorination, and sparks from short circuits. Figure 3 provides a visual depiction of this concept in a schematic form. When an electrolyte solution is introduced, the iron undergoes a process where it relinquishes its electrons, consequently leading to the creation of iron ions, such as \( \text{Fe}^{2+} / \text{Fe}^{3+} \). When a current is applied to iron from the battery, it will immediately conduct it to the electrolyte, completing the circuit. The reaction between \( \text{Fe}^{2+} \) and \( \text{Cl}^{-} \), produced through the decomposition of salt \( (\text{NaCl} \rightarrow \text{Na}^{+} + \text{Cl}^{-}) \), results in the formation of iron chloride \( (\text{FeCl}_2) \), which then precipitates onto the surface of the iron. Moreover, the presence of \( \text{Fe}^{2+} \) results in the formation of \( \text{(OH)}^{-} \) through water decomposition, leading to the occurrence of corrosion. When the battery is being discharged, the corrosion products float to the solution’s surface, and after the battery is fully discharged, the iron rusts settle down on the bottom of the solution.

The progress of a battery discharge can be determined by observing this phenomenon. In addition, due to the process of the electrolysis of water, hydrogen gas \( (\text{H}^{+}+2\text{e}^{-} \rightarrow \text{H}_2) \) is produced at the negative pole of the battery. This gas then permeates through the solution and eventually is removed from it. Additionally, the absence of hydrogen gas being produced is another clear sign that the battery has completely discharged. During the discharge using the iron powder, a small fragment slipped through the space between the battery’s positive pole, causing a short circuit between the steel shell and the cap. As a result, a small portion of the iron powder became heated, leading to the ignition of a spark. The spark had the ability to melt the plastic gasket, which serves as a separator between the steel shell and the steel cap, resulting in the formation of a small hole. Through the hole, the electrolyte of the battery had the ability to dissolve into a solution.

![Figure 3. Schematic diagram of battery discharge in salt water using bed of iron particles.](image)

The battery discharge process using salt water, iron powder, and iron flakes is shown in Figure 4. The figure illustrates the battery before and after the test, along with the discharged battery and the iron flakes that were employed. At the beginning of the experiment, the solution had a transparent appearance, while small gas bubbles constantly formed and evaporated on the negative pole of the battery (Figure 4a,e). Once the test concluded, a layer of rust formed on the surface of the solution, creating a reddish-brown film that slowly descended to the bottom (Figure 4b,f). The steel cap of the battery remained uncorroded even during the discharging process through the iron powder bed (in Figure 5a). Unfortunately, there was an electrical short circuit which caused the insulating plastic gasket to melt and subsequently become punctured (Figure 4c). Upon opening the
battery, it was observed that the solution had penetrated into both the anode and cathode separators, as shown in Figure 4d. When iron flakes were used, it was observed that the battery did not generate an electric spark. In addition to the previous findings, it was observed that there was some corrosion present on the steel cap (Figure 4g). As a result of the experiment, a dark blue coating indicating the presence of iron chloride was observed on the surface of the iron flakes. This finding can be seen in Figure 4h.

Figure 4. NCA battery immersed in salt water before and after discharging using (a,b) Fe powder and (e,f) Fe flakes, (c) insulating plastic gasket damaged by short-circuit spark, (d) salt-water-wetted cathode and anode of battery, (g) positive pole of discharged battery, (h) used Fe flakes.

At regular intervals of one hour, the battery voltage was measured throughout the entire duration of the battery discharge test. Figure 5a shows the relationship between time and the rate of battery discharge, demonstrating a curve. As shown in Figure 5a, the voltage of the battery showed a decline to 3.6 V after a period of 2 h in salt water with iron powder. Following that, it decreased even further to 3.33 V after an additional hour. The residual voltage, when measured 4 h after discharge, had decreased to the level of 0.04 V. Furthermore, after 5 h, it was observed to be approximately 0.01 V. On the other hand, the battery’s voltage, which had been maintained after 5 h of discharge using iron flakes, gradually reduced to as low as 3.5 V. Once again, the measurements were taken at hourly intervals and recorded as follows: it dropped to 3.45 V, and then further decreased to 3.31 V, and finally reached a low of 2.11 V. Furthermore, as the measurement period extended to 8, 9, and 10 h, the battery’s residual voltage steadily decreased, reaching levels of 1.2 V, 1.15 V, and 1.03 V, respectively. Despite the ongoing test, it had to be prematurely concluded after 12 h as the battery’s voltage fell to 0.007 V. The absence of hydrogen gas bubbles being released from the negative pole of the battery explains the consistent and complete drop in battery voltage. This observation indicated that the evaporation of hydrogen gas was significantly reduced when the residual voltage of the battery reached approximately 1 V.

The assessment of battery discharge efficiency is based on the percentage of residual voltage and the voltage drop. The battery’s residual voltage percentage ($E_t$) was determined by calculating the difference between the residual voltage after the discharge test and the initial voltage, as described in Equation (1). Additionally, Equation (2) was utilized to calculate the percentage of the voltage drop ($E_r$) [34].

$$E_t = \left( \frac{V_t}{V_0} \right) \times 100\%$$  \hspace{1cm} (1)

$$E_r = \left( 1 - \frac{V_t}{V_0} \right) \times 100\%$$  \hspace{1cm} (2)

where $V_t$ is the residual voltage at final time $t$ and $V_0$ is the initial voltage.
Figure 5b illustrates the difference in the percentage of residual voltage and the percentage of the voltage drop between batteries discharged with iron powder and batteries discharged with iron flakes. Comparing the effects of immersing the battery in iron powder and iron flakes, it was found that the former resulted in a residual voltage of 0.5%, with a substantial 99.5% decrease in voltage. Conversely, the battery immersed in iron flakes exhibited a lower residual voltage of 0.2%, accompanied by a 99.8% drop in voltage. In both cases, the discharge efficiency of the battery was exceptionally high, reaching approximately 100%. However, the battery immersed in iron powder demonstrated a complete drop in voltage after approximately 4 h, suggesting that it was even more efficient.

3.2. Battery Discharge in Salt Water Using a Copper Conductor

3.2.1. Battery Discharge Using a Copper Conductor Not in Contact with the Battery

By placing the battery in the middle of a copper strip conductor with a rectangular shape, the discharge test was carried out. The battery’s poles were spaced 2, 4, and 6 mm apart without contact. The battery and the conductor were then placed in a beaker containing 20 wt.% salt water. When NaCl is dissolved in a solution, the resulting salt solution becomes a strong electrolyte with the ability to conduct electricity. The reason behind this phenomenon is that, when salt is dissolved, its ions separate, enabling them to move freely within the solution and facilitating the flow of electric charge. At the moment, the electrolyte takes on a critical role in enabling the transfer of an electric current between the positively and negatively charged electrodes submerged in the solution. The speed at which the electric current passes through the electrolyte is mainly influenced by the concentration and temperature of the solution, the current density, and the distance between the electrodes. The closer the electrodes are to each other, the shorter the distance that the current has to travel, leading to a decrease in dissipation within the electrolyte medium [37,38]. As a result, when the gap between the copper conductor and the battery is reduced, the current is able to flow more quickly, consequently speeding up the discharge process of the battery. If the gap between the battery and the copper conductor is kept at a gap of less than 2 mm during the test, it is expected that the efficiency of current transmission will increase. However, it should be noted that, in practice, it might be challenging to adjust the distance to such a small value. Moreover, there is a potential risk of direct contact and the occurrence of electric shock when the distance is not adequately maintained. Therefore, the minimum test distance was established as 2 mm.

All the processes related to discharging, both physical and electrochemical, are shown in Figure 6. The current from the battery is taken through the electrolyte by the copper conductor, resulting in a quick discharge of the battery as it creates a short circuit. Due to copper’s stronger reduction potential (Cu^{2+} = 0.34), the discharge process results in
corrosion on the nickel-plated steel cap and aluminum valve of the positive pole of the battery. The occurrence of intense corrosion on the steel cap and aluminum valve led to the metals being dissolved into the solution, as can be seen in the schematic of the discharge process (Figure 6). Consequently, the electrolyte, as well as the elements present in the anode and cathode poles, emerged from the battery and proceeded to dissolve within the salt water. The salt water became contaminated due to the generation of sufficient precipitates as a result of the dissolution. The metals present, including copper, iron, nickel, and aluminum, underwent reactions with both oxygen and chlorine. As a result of these reactions, precipitates in the form of oxide and chloride compounds were formed and eventually settled at the bottom of the beaker. Hydrogen gas was formed and evaporated from the salt water as it underwent reduction at the negative pole of the battery.

**Figure 6.** A schematic of the discharging process using a copper conductor without contact with the battery.

As shown in Figure 7, one can observe the correlation between the size of the gap and the decrease in the voltage of the battery. After the first 5 h, there was a decrease in voltage to approximately 3.5 V across all gaps, and the battery’s steel cap corroded and disappeared, as illustrated in Figure 7a. As time passed, the voltage consistently diminished over 15 h, and then, at the 24 h mark, it decreased to 0.05 V at 2 mm, 0.08 V at 4 mm, and 0.12 V at 6 mm. During the discharge test with a 2 mm gap, the voltage decreased faster compared to the other tests. By performing discharge tests with different gaps, it became evident that the presence of the copper conductor amplified the voltage drop of the battery within the salt water solution. The percentage of residual voltage and the voltage drop after battery discharge, depending on the gap value, are illustrated in Figure 7b. The gap value refers to the space between the end of the copper conductor and the poles of the battery, when they are not in contact with each other. The drop in battery voltage reached its peak with the 2 mm gap, with a value of 98.7%. However, as the gap increased to 4 mm, the voltage drop decreased to 96.9%. At a gap of 6 mm, the voltage drop further decreased to 94.8%. The residual voltage percentage showed a decrease of 1.3% when the gap was reduced to 2 mm compared to gaps of 4 and 6 mm. At a maximum, the residual voltage was found to be 5.16%. Consequently, the battery’s discharge, when not in contact with a copper conductor in salt water, can decrease by more than 95%.
Figure 7. Battery discharge (a) rate and (b) efficiency, shown by percentage of residual voltage and voltage drop using copper conductor not in contact with battery.

The images in Figure 8 show the copper strip that was used for the conductor, the battery that was discharged, the solution that was contaminated, and the anode and cathode foils, with their battery components, after the test. The end of the copper strip placed near the negative pole of the battery (Figure 8a—left side of copper strip) underwent an electrochemical reaction, resulting in the formation of a white spot. On the other end of the copper strip, a group of anode and cathode elements formed, situated next to the positive pole (Figure 8a—right side of copper strip). The presence of anode and cathode elements caused the solution to become highly contaminated, resulting in a black solution (Figure 8b). We examined how the elements of the anode and cathode foils dissolved after being removed from the disassembled battery, and how this dissolution occurred through the hole that was created due to the corrosion of the steel cap. Figure 8c provides a visual representation of the stretched foils of both the anode and cathode, which can be seen as they were separated from the disassembled battery. Upon examination, wash marks were observed on the edges of both the anode and cathode foils, suggesting exposure to the solution. Despite achieving a 95% voltage drop during battery discharge, the salt water solution used, with a non-contacted copper conductor, was heavily polluted with battery elements and they persisted for an extended period of the discharging time.

Figure 8. (a) Used copper strip conductor, (b) solution, and (c) anode and cathode foils of discharged battery.
3.2.2. Battery Discharge Using a Copper Conductor in Contact with the Battery

The battery was set up with a positive pole positioned vertically at one end of the rectangular copper conductor. The negative pole was placed with a gap of 2, 4, or 6 mm from the other end of the copper strip conductor. The setup was placed in a beaker filled with 20 wt.% salt water, as shown in Figure 9. The moment the short circuit occurred, causing a connection between the (−) pole and the end of the copper conductor through the electrolyte solution, the battery discharge began with electrochemical reactions. No signs of corrosion were observed on the stainless steel cap and aluminum valve, which were connected directly to the copper conductor and experienced no electrochemical reactions on the positive pole. A process occurs whereby copper, acting as a conductor, experiences electron loss and subsequently transforms into Cu²⁺ ions when an electric current is introduced. These copper ions then react with oxygen and chlorine in the salt solution, resulting in the formation of oxides and chlorides. These reaction products are then precipitated in the solution. During the initial stage of the discharge process, the copper chloride initially floats on the surface of the salt water. However, upon exposure to air, it gradually settles to the bottom and transforms into copper hydroxide. Hydrogen gas is generated at the (−) pole of the battery, while gases evaporate from the solution. The discharge process of the battery involves chemical and electrochemical reactions that resemble the equations described in the schematic diagrams (Figures 6 and 9).

![Diagram illustrating the process of battery discharge using a copper conductor immersed in salt water.](image)

As previously stated, during the discharge process of the battery, there were green-colored reaction products that floated on the surface of the solution. These products could possibly be copper chloride (as shown in Figure 10). While these chlorides were being actively formed, they did not accumulate in significant quantities. When the chlorides reacted with the water in the solution, for example, the reaction of CuCl₂ + H₂O = Cu(OH)₂ occurred; they precipitated as copper hydroxide and settled at the bottom of the beaker. The reason why copper chlorides were not observed on the surface of the solution was due to the intense drop in battery voltage, which resulted in a decrease in the formation of chlorides. Following the discharge, the solution underwent a color change, turning from its original hue to a vibrant yellow. Additionally, a significant quantity of precipitate formed and settled at the base of the beaker, as depicted in Figure 10b.
The relationship between the voltage drop and the gap between the battery and the copper conductor can be observed in Figure 11. During the initial 5 h period, the voltage exhibited a significant drop across all gaps, reaching approximately 3.5 V, as shown in Figure 11a. This outcome closely resembled the results observed during the discharge test involving a copper conductor with no contact. Following that, the voltage steadily decreased, with the discharge rate varying based on the gap value. When the discharge test was carried out using a 2 mm gap, it was noticed that the voltage decreased significantly faster compared to the rest of the tests, eventually plummeting to a mere 0.01 V within 8 h. Over the course of 8 h, the voltage in the 4 mm discharge gap steadily decreased and eventually dropped to 0.45 V. However, even with a discharge gap of 6 mm, the voltage drop began at a relatively slow rate, after 6 h, and eventually stabilized at 0.5 V after 8 h. The graph shows that the discharge is better when the gap value is smaller. According to the graph (Figure 11b), the efficiency of the discharge test which involved a copper conductor and a battery varied based on the gap value. The voltage drop percentage increased as the gap size decreased and decreased as the gap size increased. The voltage drop at a gap of 2 mm was measured to be 88.9%, whereas at 4 mm the drop was slightly lower, at 88.2%. Similarly, at a gap of 6 mm, the voltage drop decreased further to 86.8%. In contrast, the percentage of the residual voltage differed significantly at different distances, with a lower value of 11.1% observed at 2 mm and a higher voltage drop of 13.1% recorded at 6 mm. The gap value had an impact on the battery’s discharge, resulting in its depletion.

3.3. Theoretical Framework for Discharging Process

Several studies such as those of Zheng et al. [32], James et al. [31], Jiefeng et al. [29], and Tennakone et al. [39] have reported that when a battery is discharged in salt water,
there is an electrolyte circuit that involves electrochemical reactions. According to research, the battery's voltage drop is a result of water electrolysis, which generates hydrogen gas. This is indicated by the formation of hydrogen bubbles at the negative pole. When applying a voltage above 1.23 V, water electrolysis takes place, resulting in the dissociation of water. The anode and cathode are supported by Equations (3) to (5), indicating the occurrence of electrochemical reactions.

Anode:

\[
2\text{H}_2\text{O} - 4e^- \rightarrow \text{O}_2(g) + 4\text{H}^+ \quad E^\circ = 1.23 \text{ V (3)}
\]

Cathode:

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g) \quad E^\circ = 0 \text{ V (4)}
\]

Total reaction:

\[
2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \quad E^\circ = -1.23 \text{ V (5)}
\]

The Eh–pH diagram provides a visual representation of the thermodynamic stable region of water decomposition, making it easier to understand the process of water electrolysis. The relationship between the electrochemical potential scales (Eh) and the pH level is illustrated in Figure 12, indicating a decreasing trend in the Eh for water electrolysis as the pH level increases. The diagram clearly illustrates that the green dashed line represents the water dissociation occurring in 20 wt.% salt water with a pH of 10.46. Interestingly, this dissociation process can be initiated at remarkably low voltages, specifically below the 1.0 V threshold. Explaining the battery discharge process in salt water with an iron bed or a copper conductor at room temperature is possible through the Eh–pH diagram, which provides information about the oxidation states of the elements in the Fe-Na-Cl and Cu-Na-Cl systems. Each of the diagrams is comprised of different areas, with each area symbolizing a particular locally predominant species. According to the information presented in Figure 12a, it can be observed that, in salt water with a pH of 10.5, iron exists in its Fe\(^{2+}\) oxidation state. In this environment, Fe\(^{2+}\) ions can undergo oxidation through a series of steps, namely Fe\(^{2+}\)→FeO·OH→Fe\(_3\)O\(_4\)→Fe(OH)\(_2\), which occur in the direction of decreasing electrochemical potential. The discharge phase reveals that iron is situated within the oxidation region of Fe\(_3\)O\(_4\), indicating its presence. Simultaneously, the process of NaCl decomposition occurs, resulting in the formation of Na\(^+\) and Cl(g), both of which reach a stable state. The oxidation states of copper can vary depending on the pH level of the solution when the battery is discharged with salt water and using a copper conductor, as shown in Figure 12b. The oxidation state transition of copper from Cu\(^{2+}\) to CuO→CuCl occurs in salt water with a pH of 10.5, with the electrochemical potential decreasing as the transition progresses. Na\(^+\) and Cl(g) are generated through the decomposition of NaCl, and, simultaneously, the decrease in the pH level of the solution drives the chlorination of copper, CuCl→3Cu(OH)\(_2\)→CuCl. The reaction in the solution is intensified by the presence of chlorine, which leads to the formation of CuCl\(_2\) from Cu\(^{2+}\) and Cl\(^-\). By referring to the Eh–pH diagram for Fe-Na-Cl and Cu-Na-Cl systems, it becomes feasible to provide a straightforward explanation for the processes involved in iron and copper corrosion, as well as copper chlorination.
In addition to the water splitting reaction, there were two other reactions that happened during the discharge process, which were the corrosion reaction of the metals and the decomposition reaction of the salt. The roles played by iron and nickel, which were derived from the cap; aluminum, originating from the valve of the battery; and copper, sourced from the copper conductor, were crucial in the electrochemical reactions. The reactions from (6) to (15) listed below represent the redox reactions of the elements that take place at both the anode and the cathode. Metals undergo oxidation when exposed to the oxygen generated from the process of water splitting. Additionally, the oxides formed as a result of this reaction precipitate and settle at the bottom of the beaker, as illustrated by Equations (16) and (18). Due to the process of salt decomposition, copper underwent a
reaction with chlorine, as represented by Equation (17), resulting in the formation of copper chlorides. These copper chlorides were then observed to be floating on the surface of the solution. 

Anodic half reaction:

\[
\begin{align*}
Fe - 2e^- & \leftrightarrow Fe^{2+} & E^o = 0.47 \text{ V} \\
Fe - 3e^- & \leftrightarrow Fe^{3+} & E^o = 0.037 \text{ V} \\
Ni - 2e^- & \leftrightarrow Ni^{2+} & E^o = 0.257 \text{ V} \\
Al - 3e^- & \leftrightarrow Al^{3+} & E^o = 1.662 \text{ V} \\
Cu - 2e^- & \leftrightarrow Cu^{2+} & E^o = 0.34 \text{ V} \\
2Cl^- - 2e^- & \leftrightarrow Cl_2(g) & E^o = -1.35 \text{ V} \\
Na - e^- & \leftrightarrow Na^+ & E^o = -2.71 \text{ V}
\end{align*}
\]

Cathodic half reaction:

\[
\begin{align*}
2H_2O + O_2 + 4e^- & \leftrightarrow 4OH^- & E^o = 0.82 \text{ V} \\
Cu^{2+} + 2e^- & \leftrightarrow Cu & E^o = 0.34 \text{ V} \\
Ni^{2+} + 2e^- & \leftrightarrow Ni & E^o = -0.23 \text{ V}
\end{align*}
\]

Chemical reaction:

\[
\begin{align*}
Me^{n+} + nOH^- & \rightarrow Me(OH)_n \\
Me + Cl_2 & = MeCl_2 \\
Me^{n+} + 2H_2O + ne^- & \rightarrow MeOH_n + 2H^+
\end{align*}
\]

3.4. Chemical Analysis of Precipitates

Following the discharge tests, which involved Fe flakes and a copper conductor both with and without contact with the battery, the solution was filtered. The filtered precipitate underwent a drying process for 3 h at 100 °C and was then subjected to a XRF and XRD analysis in order to identify its chemical compounds. In the discharge, Fe-01 precipitates were identified, which were generated during the discharge with Fe flakes. Cu-01 was generated in the discharge without any contact between the copper conductor and the battery, whereas Cu-02 was formed when direct contact was established between them. Table 2 presents the chemical composition of the analyzed precipitates, obtained using XRF analysis. Upon analysis, it was found that the Fe-01 precipitate was predominantly composed of FeO₃, with a detectable Cl content of 2.43%, indicating the presence of FeCl₂. The XRF analysis method exclusively measures the element's concentration and provides the results in the commonly used oxide form. Moreover, XRF analysis does not have the capability to identify the different oxidation states of elements, instead providing results solely for the most prominent oxide form. Fe exists in different oxidization states, such as FeO, FeO₂, and FeO₃. However, the Fe K-alpha peak is specifically observed in the FeO₃ state [40]. Thus, utilizing XRD analysis allows for the convenient identification of the specific oxides and phases present in the material. The Cu-01 precipitate consists of several main elements, including FeO₃, Al₂O₃, Na₂O, and Cl. Relatively small amounts of CuO, NiO, P₂O₅, and S are present in the precipitate. The Cl content here is approximately 23 wt.%, indicating the potential existence of FeCl₂ and NaCl in the precipitate. Despite
the discharge, the copper conductor showed no signs of corrosion, as evidenced by the small amount of CuO (1.69 wt.%) present. The battery cap and valve were corroded and dissolved in the solution, as evidenced by the 21 wt.% of Al₂O₃ and 34 wt.% of Fe₂O₃. In addition, phosphorus was found in the precipitate, indicating that the electrolyte (LiPF₆) of the battery might have dissolved into the solution. However, upon analyzing the precipitate of Cu-02, it was found that it had approximately 82 wt.% of CuO and 11 wt.% Cl. The suggestion is that the anode and cathode elements did not dissolve into solution, but rather that the copper conductor corroded excessively during the discharge. The precipitate’s composition, rich in CuO and Cl, indicates that it consists primarily of copper oxides and chlorides.

Table 2. The chemical composition of precipitates by XRF analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe₂O₃</th>
<th>Cl</th>
<th>Al₂O₃</th>
<th>MnO</th>
<th>CuO</th>
<th>Cr₂O₃</th>
<th>Cu₂O</th>
<th>Na₂O</th>
<th>NiO</th>
<th>SO₃</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-01</td>
<td>95.99</td>
<td>2.43</td>
<td>0.79</td>
<td>0.45</td>
<td>0.21</td>
<td>0.12</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu-01</td>
<td>31.43</td>
<td>23.06</td>
<td>20.88</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.69</td>
<td>22.13</td>
<td>0.53</td>
<td>0.10</td>
<td>0.16</td>
</tr>
<tr>
<td>Cu-02</td>
<td>2.82</td>
<td>11.48</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>82.26</td>
<td>2.83</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The XRD analysis determined the composition of the precipitates of Fe-01, Cu-01, and Cu-02. This analysis also confirmed the corresponding data of PDF No, as shown in Figure 13. The XRD pattern displays the intensity line of each phase’s data in varying colors at the bottom. The Fe-01 precipitate which was analyzed was determined to primarily consist of the Fe₃O₄ phase. This phase has been identified as corresponding to PDF No 03-065-3107. Fe₂O₃ consists of a combination of Fe²⁺ and Fe³⁺ ions, and it can be written as FeO·Fe₂O₃ in some instances [41–43]. The iron rust Fe(OH)₂ that formed during the discharge process may have transformed into an FeO·Fe₂O₃ state after drying. The XRF analysis confirms the findings of the XRD analysis, indicating that the Fe-01 precipitate contains approximately 96 wt.% Fe₂O₃ oxide. Additionally, it should be noted that there was the detection of a small amount of iron phase (PDF No 03-065-4899), indicating the potential occurrence of a small piece of iron breaking off from the iron flakes. The presence of an iron phase in the precipitates suggests that it may have been combined with iron particles originating from the powdered iron. The reason for the undetected FeCl₂ phase in the Fe-01 precipitate could be attributed to its low Cl content. However, the Cu-01 precipitate contained both NaCl (PDF No 00-005-0628) and FeCl₂ (PDF No 01-085-1438), with NaCl being the predominant compound. An XRF analysis does not provide the means to ascertain the composition of chloride compounds. However, Cl was independently determined and, in the XRD analysis, Na and Fe were detected as compounds along with chlorine and identified as their respective oxides. The composition of the sediment, with around 31 wt.% iron (Fe), 22 wt.% sodium (Na), and 23 wt.% chlorine (Cl), indicates that their compounds likely make up the major constituents of the Cu-01 precipitate. The undetected compounds in the precipitate were not identified because of their small content. The XRD analysis revealed that, in the Cu-02 precipitate, there was a higher concentration of copper oxychloride (Cu₂Cl(OH)₃ with PDF No 00-050-1559) and cuprous oxide (Cu₂O with PDF No 01-078-2076). The results of the XRF analysis of the Cu-02 precipitate indicated that approximately 82 wt.% of the composition is copper oxide, while 11 wt.% is chlorine, which aligns with the findings from the XRD analysis that suggest the presence of copper chloride and copper oxide phases. All the results obtained from the XRD analysis were in complete agreement with this proposition, which was based on the findings of the XRF analysis of the precipitate’s chemical composition. Alternatively, the results from both analysis methods confirmed each other.
3.5. Comparing Battery Discharge Approaches in Electrolyte Solution

The results of the battery discharge tests in various electrolyte solutions are summarized in Table 3. Among the various solutions examined in these studies, it was found that the NaCl solution demonstrated the highest discharge capacity, making it the most effective solution. It was confirmed through experiments that the discharge rate showed an increase when the concentration of the NaCl solution exceeded 5%. On the downside, the corrosion of the battery components became more severe in this salt solution, which is its disadvantage. In their study, Mohammad et al. [34] utilized copper wire electrodes to carry out the discharge process, aiming to prevent corrosion. This approach allowed them to avoid the need for direct immersion of the battery in the salt solution. The battery was completely discharged in a solution containing 20% NaCl; however, it was noted that the presence of corrosion on the copper electrode posed challenges during the testing process. Additionally, Severi et al. [35] discovered that the most efficient discharge occurred when utilizing Pt wire electrodes submerged in a NaCl solution containing Fe and Zn metal beds, as opposed to other salt solutions like MnSO₄, ZnSO₄, and FeSO₄ at concentrations ranging from 5% to 20%. This research work has a unique feature, as the battery voltage experienced a complete drop in just 4.4 h when Pt wire electrodes were connected to the zinc powder and iron flakes. However, the Pt wire electrode is not cost-effective for direct use in practical applications and is limited by the extra effort needed to connect it to the battery. Our research work stands out due to its unique approach of immersing the battery directly in the salt solution, without the need for additional electrodes, and utilizing a metal accelerator to prevent corrosion and rapidly decrease the battery voltage. Furthermore, extensive testing has demonstrated that the use of an iron powder bed results in a slightly faster discharge rate than that in these studies. Additionally, it is worth mentioning that once the battery discharge process is complete, a crucial step involves filtering the precipitate that forms in the solution. The solution that has been filtered is then reused for the purpose of discharging. Due to its high quality, it is more convenient to process and market the separated precipitates alongside the iron and copper products, which have a high consumption rate. Upcoming research will propose an optimal solution by leveraging experimental data to effectively convert the precipitates formed during the discharge into valuable products.
Table 3. Battery discharge approaches in salt solutions.

<table>
<thead>
<tr>
<th>Electrolyte Solution</th>
<th>Accelerator</th>
<th>Discharge Efficiency</th>
<th>Discharge Timing</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% NaCl</td>
<td>Fe powder and flakes, Cu strip</td>
<td>~100%</td>
<td>within 4 h, over 8 h</td>
<td>Erdenebold et al.</td>
</tr>
<tr>
<td>NaCl, Na2CO3, Na2SO4, and MnSO4</td>
<td>Copper powder, graphite flakes</td>
<td>~94%</td>
<td>within 4 h, over 8 h</td>
<td>Hao et al. [19]</td>
</tr>
<tr>
<td>5% K2CO3, 5% Na2CO3 at 50 °C</td>
<td>Steel staples</td>
<td>~0.5 V</td>
<td>4–5 h</td>
<td>Nicole [36]</td>
</tr>
<tr>
<td>5–10% NaCl, NaOH, 1–2 mol/L MnSO4, 0.4–1.2 mol/L NaCl, MnSO4, ZnSO4, and FeSO4</td>
<td>Pt wire electrodes no</td>
<td>~0.25 mAH</td>
<td>within 20 h</td>
<td>Jiefeng et al. [29]</td>
</tr>
<tr>
<td>&gt;5% NaCl, NaOH, NaNO2, K2CO3, NH3, NaHSO4, Na2CO3, KBr, (NH4)2CO3, and NH4HCO3</td>
<td>Steel staples no</td>
<td>&gt;75%</td>
<td>10 h</td>
<td>James et al. [31]</td>
</tr>
<tr>
<td>5–20% NaCl, MnSO4, ZnSO4, and FeSO4</td>
<td>Fe flakes, Zn powder Pt wire electrodes</td>
<td>Completely</td>
<td>4.4 h</td>
<td>Severi et al. [35]</td>
</tr>
<tr>
<td>12–20% NaCl, Na2S, and MgSO4, 25–60 °C</td>
<td>Cu wire electrodes</td>
<td>Completely</td>
<td>2–10 h</td>
<td>Mohammad et al. [34]</td>
</tr>
</tbody>
</table>

4. Conclusions

The testing involved two different methods for discharging an NCA battery (3.78 V) in common salt water. One key distinction that sets these apart from other approaches is the rapid drop in battery voltage during the first step. This drop is caused by creating a short circuit when the positive pole of the battery is submerged into the metal particles in the electrolyte solution. An important aspect to highlight is that the positive pole components of the battery are safeguarded against corrosion throughout this process. Another approach to lowering the battery voltage is to employ copper conductors in a highly intensive manner. Based on the studies conducted by Severi [28] and Mohammad [27], a 20 wt.% NaCl solution was employed for the experiment. The results of the experimental work can be summarized by the following observations:

- The objective of this method was to study how iron powder and flakes affect battery voltage, and specifically their ability to reduce it. In the case of a battery immersed in iron powder, the discharge rate was 99.5% within the first 4 h. However, the use of iron flakes resulted in a voltage drop of 99.8% after a longer duration of 12 h. Through this method, it was found that the voltage could be decreased without causing any corrosion to the components of the battery.

- One of the drawbacks associated with this method is the susceptibility of iron to oxidation and chlorination reactions during the discharge process, leading to the contamination of the solution with precipitates primarily composed of iron Fe3O4 oxides. However, it has been suggested that by repurposing the extremely fine iron oxide into a by-product, the economic benefit can be significantly boosted.

- By employing the second technique, the battery was discharged through a process that entailed both contacting and not contacting the copper conductor with the battery. In cases where there was no contact, it was observed that the battery’s steel cap and aluminum valve tend to corrode easily, leading to the dissolution of the anode and cathode elements into the solution, thereby causing pollution. Due to these reasons, this particular method was considered inconvenient. Conversely, in situations where only the positive pole of the battery was in contact with the copper conductor and the other end of the conductor was placed at gaps of 2, 4, or 6 mm from the
negative pole, there was no evidence of corrosion present in any of the battery components. Contrary to expectations, it was found that the copper conductor on the negative pole of the battery had undergone corrosion. Within 8 h, this method caused the battery voltage to drop to approximately 90%. As the gap size decreased, it was verified that the discharge rate tended to increase.

- Through the utilization of XRF and XRD analyses, it was confirmed that CuCl₂·3Cu(OH)₂ and Cu₂O compounds were present, indicating that these compounds were generated and precipitated in the solution due to the corrosion of copper. This precipitate has the potential to transform and produce copper by-products with practical uses.

- This study focused on explaining the oxidation states of elements in the Fe-Na-Cl and Cu-Na-Cl systems, and specifically those that are locally predominant. This was achieved by utilizing the theoretical framework provided by the Eh–pH diagram and electrochemical reactions, which were based on the HSC-62 Chemistry database. The intention is for the reader to gain a better understanding of these new methods by presenting them in a wider context.

The authors propose that, in the future, it may be feasible to conduct research on the implementation of a method that involves using ordinary seawater and steel bulks or scrap copper strips to discharge large numbers of cylindrical batteries for practical applications.

**Author Contributions:** E.U.: Methodology, Data curation, Investigation, Writing—original draft, Data curation, Software, Validation; J.-P.W.: Project administration, Conceptualization, Writing—review and editing, Funding acquisition. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Brain Pool program [Grant Number RS-2023-0022959], which is backed by the Ministry of Science and ICT through the National Research Foundation of Korea, this research was successfully conducted.

**Data Availability Statement:** The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

**Conflicts of Interest:** The authors declare no conflicts of interest.

**References**


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