

Evaluating Aqueous Electrolyte Effects on the Electrochemical Output of Aluminum-Air Batteries

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ABSTRACT

As the global energy demands continue to increase, there is an immediate need for advanced battery materials. This paper examines the influence of different aqueous electrolytes and their concentration on the electrochemical characteristics of aluminum-air batteries. A recycled lab cell was designed using technical-grade aluminum and carbon and tested with sodium chloride, sodium sulphate, sodium benzoate, sodium hydroxide, and potassium hydroxide (0.05 to 2.0 M), and the results show that potassium hydroxide yields the highest open-circuit voltage of 1.49 V because of its high ionic conductivity, whereas sodium sulphate does not display a significant hydrogen evolution reaction but instead exhibits a steady potential of 1.10 V. Higher concentrations enhance conductivity but accelerate anodic corrosion. Moreover, sodium benzoate is an organic additive that suppresses self-discharge with low voltage output. The results of these studies give a basis to optimize the composition of electrolytes to balance electrochemical performance and anodic corrosion in high-energy-density storage systems.

Keywords - Aluminum Air Batteries, Aqueous Electrolytes, Electrochemical Potential, Anodic Corrosion.

1. INTRODUCTION

The rising world energy demands, as seen by a 2.2% growth in the year 2024, with the future CO₂ emissions projected to reach around 38.1 Gt of CO₂ in the year 2025 [1][2], show that there is an urgent need for sustainable energy and low-carbon energy solutions. The modern world cannot do without batteries, which suit a vast range of uses, such as motor vehicles, handheld electronics, and biomedical devices [3].

Modern lithium-ion batteries, while dominating the market with energy densities typically ranging from 240–300 Wh/kg [4][5][6], are, nevertheless, a problem since they heavily depend on the limited resources of lithium and cobalt, not to mention recycling and safety issues [3][6][7]. Despite LIB costs having declined, there remain hurdles for widespread adoption [9]. Earlier chemistries, such as nickel-cadmium batteries, have a low energy density and the so-called memory effect [10], and lead-acid batteries, notwithstanding their inexpensive nature and high prevalence in vehicles, are large and have a low energy

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density [10]. This is the reason why innovative, more efficient, and greener energy storage systems are being developed [11][7].

Metal-air batteries, such as the lithium-air, zinc-air, magnesium-air, and aluminum-air, may represent an opportunity to use atmospheric oxygen as the main cathode reactant [12]. This design offers a substantial decrease in the cell weight and the maximum active energy storage material in the cell, which helps maximize theoretical energy densities relative to LIBs [13][14][15]. The practice of using primary zinc-air cells in appliances such as hearing aids shows that the metal-air technology is practically feasible [16]. Aluminum, being abundant, lightweight, and infinitely recyclable, is a particularly attractive material for AABs, offering a cost-effective and eco-friendly energy storage solution [17][5]. AABs have fantastic theoretical performance, with a theoretical energy density of about 8.1 kWh/kg [8][18][19] and a theoretical cell potential of 2.7 V [12] in alkaline electrolytes.

Despite these benefits, the high commercialization of AABs is hindered by several key challenges. Aluminum anodes readily form a protective oxide layer in air and aqueous environments, which increases corrosion potential, self-discharge, and dissolution rates, ultimately decreasing the energy density [17]. Further performance degradation is caused by self-corrosion, passivation, and parasitic hydrogen evolution reactions in aqueous electrolytes [20][21]. The primary issues that prevent AABs from being rechargeable include anode corrosion, low discharge rates, high self-discharge rates, and irreversibility [22][19]. Using concentrated potassium hydroxide or sodium hydroxide solutions can improve electrochemical performance, but this comes at the expense of aluminum corrosion [23]. Rechargeable AABs require the creation of superior alloys or corrosion inhibitors, but electrochemical reversal by mechanical recharging, i.e., by replacing the anode, is a practical alternative to complex electrochemical reversal.

Available studies have emphasized the importance of the formulation of electrolytes in countering these difficulties [23][24]. Although strong alkaline systems increase the conductivity, they also enhance corrosion, and this may be a serious trade-off [17]. There are limited comparative performance studies of AABs in neutral or weakly acidic electrolytes. Even though it may be used as a reaction facilitator, sodium chloride results in reduced voltage and current output in general. Moreover, the capabilities of using sulphate or organic buffers, e.g., sodium benzoate, are not thoroughly investigated, and few head-to-head comparisons of the traditional use of KOH or NaOH electrolytes have been done under the same operating conditions.

To fill these research gaps, the proposed project will assess the electrochemical performance of the waste and scrap-materials-based fabricated aluminum-air cells, which are cost-effective and lightweight and can be used as a substitute for the existing Li-ion and other technologies. The experimentation is methodically investigating the effects of the five different electrolytes at different concentrations. This research keeps the effect of the electrolyte composition on the critical performance parameters constant by maintaining the same cell design, anode made of aluminum, and cathode made of carbon. The final objective is to find the initial open-circuit voltage and peak discharge current as a function of time, with the objective of identifying the best electrolyte conditions that provide better voltage and performance of the battery.

2. MATERIALS AND METHODS

2.1 Materials

All materials used in this study were of analytical or laboratory grade and procured from certified commercial suppliers (Amazon India and ibuychemikals). Material selection was based on electrochemical stability, physicochemical properties, availability, and compatibility with the experimental design.

2.1.1 Carbon Rod

High-purity carbon rods (40 × 29 × 22 mm; Mata Mandanan Enterprises) were employed as cathode current collectors due to their high electrical conductivity, chemical inertness, and resistance to corrosion in aqueous electrolytes.

2.1.2 Aluminum Chimney

An aluminum chimney (length: 10 feet; diameter: 4 inches; Kavita Corporation) was used as the sacrificial anode and structural component of the cell. Aluminum was selected for its high electrochemical reactivity, low density, and ease of replacement following corrosion.

2.1.3 Electrolytes

The electrolytes evaluated in this study included sodium chloride (≥99%; Isochem Laboratories), sodium benzoate (≥99%; Isochem Laboratories), sodium hydroxide (≥98%; Advent Chembio Pvt. Ltd.), potassium hydroxide (≥99%; Pure Chemicals Co.), and sodium sulphate (≥99%; HiMedia).

2.1.4 Miscellaneous

Polyvinyl chloride (PVC) pipes (diameter: 4 inches; length: 6 inches) served as the external housing of the electrochemical cell. Matching plastic end caps were fitted at both ends and sealed to prevent electrolyte leakage and evaporation.

A neutral-cure transparent silicone sealant (operating temperature range: -40 °C to 150 °C; ABRO Industries USA) was used to ensure watertight and airtight sealing at all junctions and to provide mechanical insulation for electrode mounting.

2.2 Strategy for Electrolyte Concentration Selection

The selected molarity values were based on findings from the literature, which showed that increasing electrolyte concentration can improve ionic conductivity and power output but may also increase reaction severity and corrosion. The same molarity values were used for all salts to ensure a fair and consistent comparison of their electrochemical performance under identical concentration conditions. [19][25][26]; the corrosive conditions of these solutions result in corrosion of the aluminum anode [27]. Initial tests on this experiment showed that, at concentrations above 3.0 M, the whole of the aluminum structural parts were consumed in a minimal period of time, with severe gassing of hydrogen and expansion of the

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electrolyte volume, which did not allow longitudinal performance to be observed. Therefore, the selectivity in the concentration of electrolytes was aimed at a slender zone between 0.05 M and 2.0 M. The selection of this range was to make the anode material not depleted at the same time; hence, the opportunity to record the measurement of Open Circuit Voltage (OCV) in a systematic way in a five-day observation period. This choice can provide adequate ionic strength to determine concentration-dependent trends in kinetics and still allow for the structural integrity of the cell to be compared.

2.3 Electrolyte Preparation

Aqueous electrolyte solutions were prepared at concentrations of 0.05 M, 0.5 M, 0.75 M, 1.0 M, 1.5 M, and 2.0 M. Each solution was prepared independently to ensure accurate molarity. The prepared electrolyte was introduced into the assembled cell until both electrodes were partially submerged. This approach enabled evaluation of concentration-dependent effects on ionic conductivity, internal resistance, and anode corrosion kinetics under constant cell geometry.

2.4 Cell Fabrication and Assembly

Sections of aluminum chimney were cut to a length of about 6 inches and inserted concentrically into PVC pipe sections of the same diameter. The bottom of the cell was made by attaching one end cap to the pipe base.

The cathode current collector was a solid carbon rod, which was mechanically fixed to the inner wall of the PVC pipe with an insulating molded sealant. The rod was suspended so that it did not contact the cell base and remained electrically isolated from the aluminum anode.

After the electrodes had been placed, internal alignment was checked to maintain the same distance between them and to eliminate physical contact. Premade solutions of electrolytes were added to the setup cell until the electrodes were sufficiently immersed. The open end of the PVC pipe was then sealed with a second end cap using silicone sealant to ensure leak-free operation.

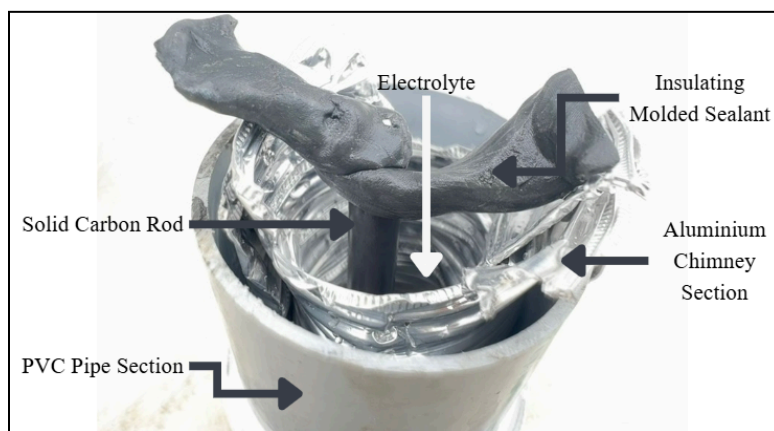


Figure 1: Internal configuration and component layout of the assembled electrochemical cell.

2.5 Experimental Setup

The electrochemical cell consisted of a PVC housing containing a concentric aluminum chimney acting as the anode and a centrally suspended carbon rod acting as the cathode current collector. The outer electrode surface was the aluminum chimney that was in direct contact with the electrolyte and could be removed and replaced in the event of corrosion. The carbon rod was not electrically connected but was immersed in the electrolyte. Electrical contacts were made at the uncovered aluminum and the carbon rod end.

2.6 Electrochemical Measurements

A digital multimeter was used to measure the open-circuit voltage of each cell between the aluminum anode and carbon cathode. Measurements were recorded once daily over a period of five consecutive days for each electrolyte and concentration. All the information was tabulated to make comparisons.

3. RESULTS AND DISCUSSION

3.1 NaCl

Table 1: Open-Circuit Potentials for Sodium Chloride (NaCl) Across a Five-Day Duration

	Molar solution of NaCl						
Day	0.05M	0.5M	0.75M	1M	1.5M	2M	Blank
Day 1	0.6	0.77	0.85	0.89	0.91	0.94	0.07
Day 2	0.62	0.8	0.87	0.9	0.93	0.95	0.08
Day 3	0.64	0.84	0.9	0.92	0.95	0.98	0.07
Day 4	0.65	0.84	0.87	0.91	0.93	0.96	0.06
Day 5	0.63	0.83	0.85	0.89	0.92	0.95	0.06
Mean Voltage	0.628	0.816	0.868	0.902	0.928	0.956	0.068

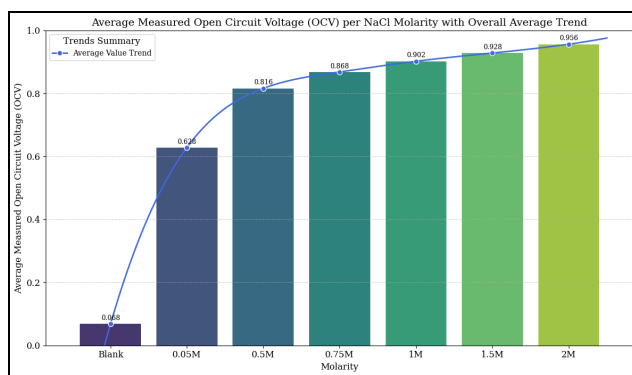


Figure 2: Voltage Trajectory and Discharge Characteristics of Aluminum-Air Cells in Sodium Chloride (NaCl)

The OCV vs. molarity curve of NaCl has a slope that resembles a logarithmic curve: the voltage rises dramatically between 0.05 M and 0.75 M and then more gradually to 2.0 M. There is a peak on Day 3 with minor decay on Days 4 and 5 in all the concentrations. In general, OCV increases progressively with molarity, with 2.0 M providing the maximum potential (maximum value of 0.98 V on Day 3). This is mainly due to improved ionic conductivity, which decreases ohmic drops across the separator and cathode pouch. Higher concentrations further boost oxide film breakdown via pitting, as these ions penetrate the layer at defects like grain boundaries, forming soluble aluminum chlorides that detach the film and expose active sites. The Day 3 peak is probably an initial conditioning step, whereby the electrolyte enters the porous graphite cathode and puts into action the oxide layer. This subsequent degradation is due to the buildup of insoluble discharge products; in the case of near-neutral NaCl, a layer of passivation on the electrodes is developed due to their low solubility, increasing ionic and oxygen diffusion resistance. This means that the deposition of these on the electrode surfaces may hinder mass transport, which causes the decline of cell performance in the long run [28]. This is also in line with the fact that, although increasing NaCl concentrations enhanced the performance of the anode by lowering the resistance to charge transportation, the fact that the discharge products accumulated with time and the reaction sites eventually became saturated inhibited sustained voltage production [29].

3.2 Na₂SO₄

Table 2: Open-Circuit Potentials for Sodium Sulphate (Na₂SO₄) Across a Five-Day Duration

	Molar solution of Na ₂ SO ₄						
Day	0.05M	0.5M	0.75M	1M	1.5M	2M	Blank
Day 1	0.67	0.92	0.97	1.02	1.09	1.13	0.04
Day 2	0.69	0.92	0.96	1.03	1.08	1.14	0.05

Day 3	0.7	0.91	0.96	1.02	1.07	1.12	0.02
Day 4	0.7	0.9	0.95	1.01	1.07	1.11	0.04
Day 5	0.69	0.88	0.94	1	1.05	1.1	0.04
Mean Voltage	0.69	0.906	0.956	1.016	1.072	1.12	0.038

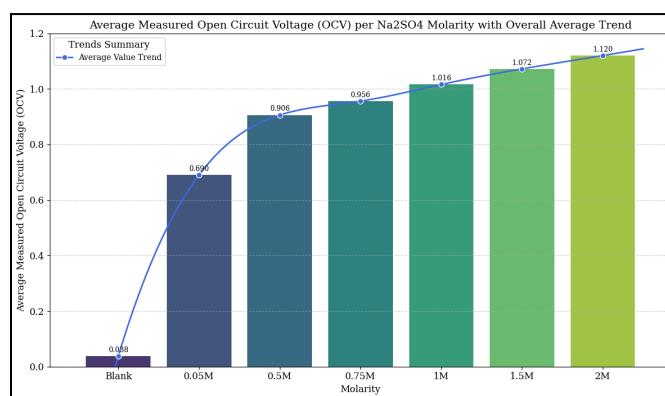


Figure 3: Voltage Trajectory and Discharge Characteristics of Aluminum-Air Cells in Sodium Sulphate (Na₂SO₄)

The OCV plotting of Na₂SO₄ shows that the OCV at the baseline is higher compared to NaCl. There is an outstanding stability of the 2.0 M series in that the series may be depicted as almost flat throughout the five-day period, with a total deviation of 0.04 V quite low in comparison to the 0.05 M series, which is significantly lower. Overall, Na₂SO₄ consistently yielded higher OCV values than equivalent NaCl concentrations, with the 2.0 M cell reaching 1.14 V.

This high voltage is presumably because SO₄ ions suppress the most limiting pitting corrosion, which ironically allows a more homogeneous and stable potential on the anode surface in relation to the unpredictable chloride-induced pitting. Temporal stability was also notable: compared to the Day 3 peak in NaCl, Day 2 gave Na₂SO₄ cells higher values that were maintained until Day 5. The voltage decreased merely between 1.14 V and 1.10 V in four days at 2.0 M, indicating that the electrochemical environment was strong. This, together with the lack of hydrogen evolution, makes sodium sulphate better as the primary Al-air cell with constant voltage requirements over long durations without the issue of alkaline corrosion. This stability is consistent with the results that sulphate-based additives are effective inhibitors of self-corrosion and hydrogen evolution, which improve the efficiency of anode utilization [30]. Nevertheless, a saline setting may lead to a lower reaction order of aluminum oxidation with correspondingly lower discharge potentials than alkaline ones [29]. Although such kinetic constraints exist, the saline electrolytes have clear safety benefits through eliminating the high-rate depletion of

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hydroxide and caustic handling challenges of the alkaline systems [19]. Moreover, the addition of sulphate ions was found to enhance the performance of discharge and the use of the anode by establishing soluble salts in the alkaline matrix, which ultimately avoids the formation of passivating layers that hinder long-term functionality [30].

3.3 C₆H₅COONa:

Table 3: Open-Circuit Potentials for Sodium Benzoate (C₆H₅COONa) Across a Five-Day Duration

	Molar solution of C ₆ H ₅ COONa						
Day	0.05M	0.5M	0.75M	1M	1.5M	2M	Blank
Day 1	0.6	0.86	0.91	0.94	0.99	1.01	0.07
Day 2	0.59	0.85	0.9	0.93	0.98	0.99	0.06
Day 3	0.58	0.84	0.89	0.92	0.95	0.98	0.07
Day 4	0.56	0.81	0.86	0.9	0.93	0.95	0.05
Day 5	0.53	0.78	0.84	0.87	0.91	0.92	0.04
Mean Voltage	0.572	0.828	0.88	0.912	0.952	0.97	0.058

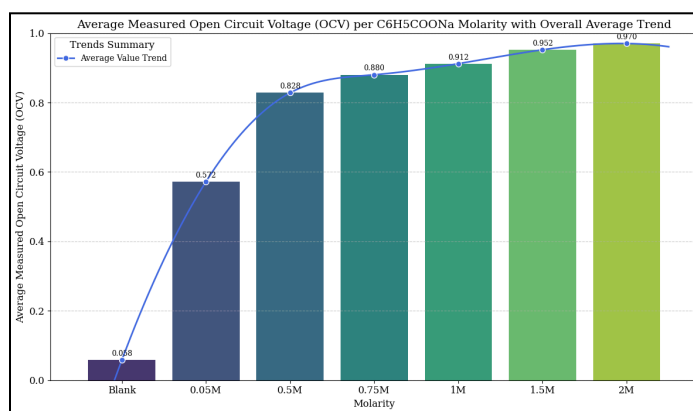


Figure 4: Voltage Trajectory and Discharge Characteristics of Aluminum-Air Cells in Sodium Benzoate (C₆H₅COONa)

The sodium benzoate curves have a negative slope throughout the concentrations. An increase in molarity causes the whole curve to be shifted upwards, but the rate of decrease in the voltage is the same, and this process gives a collection of parallel lines that slope downwards towards Day 5. In contrast with the inorganic salts, OCV peaks at a maximum of 1.01 V at 2.0 M with a steady decline during the period between Day 1 and Day 5. As an example, the cell with a concentration of 0.05 M decreased its voltage level by 11.67% (0.60 V to 0.53 V). This gradual decrease corresponds to the inhibitory effect observed in the voltage table: as the reaction continues, the benzoate anions block the active site of the aluminum anode, creating a molecular obstacle that inhibits the parasitic HER and the oxidation of the metal. The barrier becomes thicker with time through the complexes of organic and aluminum, and eventually increases the resistance of charge transfer. Although it would be a good choice in long-term stability and safety, the kinetic limitations of sodium benzoate make it an inappropriate main electrolyte in high-power uses. Its low solubility above 2.0 M also limits the voltage gain from higher concentrations. Conversely, the fast oxide layer dissolution by the alkaline electrolytes is through the hydroxide attack, revealing a fresh aluminum surface area and allowing increased electrochemical activity [31].

3.4 NaOH

Table 4: Open-Circuit Potentials for Sodium Hydroxide (NaOH) Across a Five-Day Duration

	Molar solution of NaOH						
Day	0.05M	0.5M	0.75M	1M	1.5M	2M	Blank
Day 1	1.32	1.32	1.35	1.42	1.44	1.46	0.1
Day 2	1.33	1.33	1.34	1.44	1.45	1.45	0.09
Day 3	1.32	1.34	1.35	1.43	1.45	1.44	0.09
Day 4	1.31	1.32	1.36	1.42	1.44	1.44	0.1
Day 5	1.29	1.32	1.35	1.42	1.44	1.43	0.08
Mean Voltage	1.31	1.32	1.35	1.42	1.44	1.44	0.092

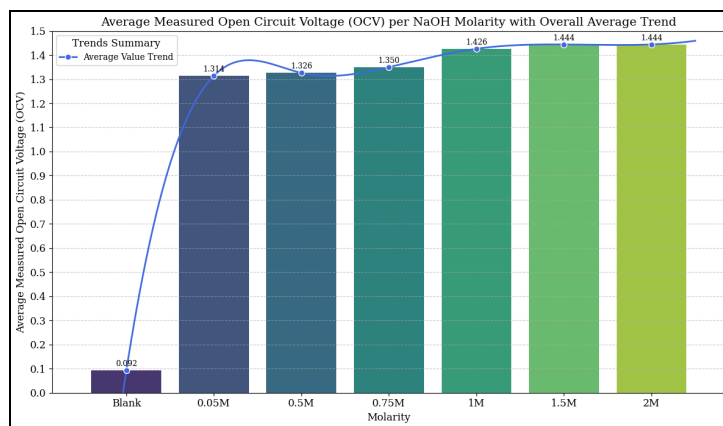


Figure 5: Voltage Trajectory and Discharge Characteristics of Aluminum-Air Cells in Sodium Hydroxide (NaOH)

The NaOH data represented a sharp increase in the OCV of 0.5 M to 1.0 M, and then the curves leveled off. Temporal stability is also superb, with the 1.0-2.0 M lines almost flat, showing that the system is fast to reach its potential limit and hold on to it. OCVs of NaOH are far higher than the neutral salts, the 0.05 M solution recording 1.32 V. Its dependence on concentration is non-linear: voltage increases with concentration between 0.5 M and 1.0 M, and then it levels off. This is due to the leveling off, as at these concentrations chemical dissolution of the oxide layer is fast enough to saturate the surface completely and the potential is reduced to that of the $\text{Al}/\text{Al}(\text{OH})_4$ couple. Stability in moderate concentrations is good over the five days, with the 1.0 M and 1.5 M cells displaying minimum variation, but the 2.0 M cell displays a slight decrease by the 5th day, probably caused by the corrosiveness of the electrolyte interfering with the uniformity of the anode. In contrast to neutral electrolytes, NaOH prevents passivation as discharge products are dissolved, and, therefore, the active surface area is preserved, and the voltage remains unchanged. Nevertheless, this violent chemical behavior also enhances the parasitic self-corrosion that may jeopardize the efficiency of using an anode regardless of the high electrochemical potential [32].

3.5 KOH

Table 5: Open-Circuit Potentials for Potassium Hydroxide (KOH) Across a Five-Day Duration

	Molar Solution of KOH						
Day	0.05M	0.5M	0.75M	1M	1.5M	2M	Blank
Day 1	1.33	1.38	1.39	1.45	1.45	1.48	0.08
Day 2	1.34	1.38	1.41	1.46	1.47	1.49	0.08

Day 3	1.35	1.37	1.41	1.45	1.48	1.48	0.07
Day 4	1.35	1.36	1.41	1.44	1.47	1.47	0.05
Day 5	1.33	1.36	1.4	1.43	1.46	1.45	0.06
Mean Voltage	1.34	1.37	1.40	1.44	1.46	1.474	0.068

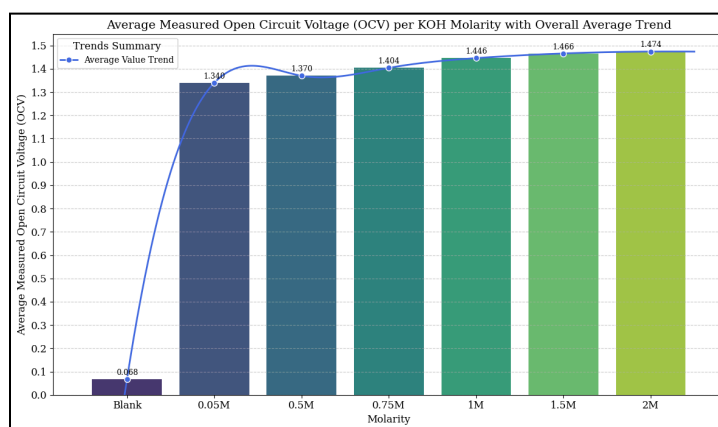


Figure 6: Voltage Trajectory and Discharge Characteristics of Aluminum-Air Cells in Potassium Hydroxide (KOH)

The overall voltage profile of KOH is higher than that of all the electrolytes tested, with the 2.0 M concentration being the highest at 1.49 V. The concentration lines of the electrolyte were more separated at 0.05-1.0 M compared to NaOH, which is less sensitive to changes in concentration. Although the KOH series recorded the greatest OCV values throughout the experiment, it was the most stable at 0.75 M and 1.5 M, with practically no degradation over a period of five days. This enhanced stability compared to that of NaOH is due to the enhanced mobility of the K ions, which deteriorates the formation of compact, non-porous, discharge product layers on the anode and enables OH ions to be continuously transported to the metal surface. Despite these advantages, reaction severity and hydrogen evolution are major limitations. Hydrogen evolution and corrosion were identified qualitatively through visible gas bubble formation on the aluminium anode and observable surface degradation of the electrode during operation. No direct measurements of hydrogen generation, corrosion rate, or electrode mass loss were performed. Though maximum OCV values in KOH are the maximum possible in an aqueous Al-air cell under the geometry used, high self-corrosion rates are probable to have low Coulombic efficiency. To render the use of Al-air batteries cost-effective with these electrolytes, future research needs to focus on the use of additives that inhibit the hydrogen evolution reaction but do not affect the excellent kinetics of KOH. The effect of organic inhibitors like sodium benzoate is to adsorb onto active anode sites to produce a protective film that reduces parasitic corrosion [19] and does not affect the high ionic conductivity

necessary to gain power density. The studies prove this approach because KOH-based electrolytes are better than NaOH counterparts because they are more ionically conductive, exhibit lower viscosity, and react more rapidly [18]. An example is that KOH had a peak power density of 142.4 mW/cm² and energy densities of 2778.40 mWh/g, and NaOH had a peak power density of 120 mW/cm² and energy densities of 2385.02 mWh/g [33]. Nonetheless, NaOH electrolytes are very sensitive to concentration since too high molarity may cause a rise in viscosity and decrease the rate of hydroxide ion transfer and thus the reaction rate [34]. On the other hand, lowered hydroxide concentration limits the concentration of reactive species on the anode interface and prematurely causes the voltage to fall and low specific capacity by ion depletion [35].

4. CONCLUSION

As a determining factor of the electrochemical efficiency of the aluminum-air batteries, this study cites electrolyte selection as the key factor. The best media proved to be potassium hydroxide, where the maximum open-circuit voltage was 1.49V. This high performance is a result of the high ionic mobility of the potassium cation, which keeps in the active reaction in the electrode interface than sodium based versions or neutral ones [36]. Even though sodium hydroxide can produce competitive kinetics, it has a higher sensitivity to change of concentration. Sodium sulphate would be an excellent substitute in applications where stability and operational safety are the main criteria. It also maintained a steady 1.14 V and avoided the violent self-corrosion and hydrogen accumulation found in caustic solutions [37]. Sodium benzoate was shown to be useful as an anode protection kinetic inhibitor, but is limited in terms of thermodynamic limitations to act as a secondary regulator and not as a primary electrolyte. There are a number of issues that limit the extent of this assessment. The cell design used here, which is the static flooded type, has the inherent problems of mass transport. The byproducts of reactions build up with time and increase the resistance within the core, reducing the rate of diffusion of the reactive species. Alternatively, the heterogeneity of the surface and impurities of alloys in technical-grade scrap aluminum were the probable factors that provided the uneven pitting in saline conditions [38]. These findings indicate that in practice, interfacial fouling limits such systems, but not the theory of energy density. One limitation of this study was that each electrolyte and concentration condition was tested only once. Consequently, statistical estimates of experimental variability were not possible, and reported values were single observations. The observed trends offer valuable initial information, but further studies should include replicate experiments and uncertainty analysis to enhance the robustness of the conclusions. The next step in the development of such systems will be the transition to hybrid electrolyte engineering. Namely, the introduction of small doses of organic inhibitors into a potassium hydroxide bulk would allow the mitigation of parasitic responses without any reduction of the power density [36]. Another obvious way to go is the creation of flow-based architectures. The active circulation of the electrolyte would carry away the precipitates and sustain a constant electrochemical gradient over longer periods of time. Lastly, it will be required to test performance with different electrical loads to provide real-world power limits of high-density portable energy storage [39].

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