Performance of Aluminium Air Battery Using Different Electrolytes and MnO₂ as a Catalyst.

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Abstract

In an open format, more than 15 aluminum air cells were tested for performance. The anode was aluminium, with different electrolyte assembly, electrolyte absorber thickness, MnO2 catalyst ratio on activated carbon, aluminium plate thickness, and cell area. Graphical interpretations are produced to compare voltage and current output experimental results. MnO2 showed unsuccessful outcomes compared to other cell assemblies, but it helped achieve the same results with 20% less NaOH. NaOH was chosen because it is inexpensive and achieves the same action with a lower concentration, extending battery life.

key words: Aluminium air battery; Basic electrolytes; Acidic Electrolyte with Basic Electrolyte; MnO₂ as catalyst;

Introduction

Energy crises, pollution control, health, and a stable economy are the primary basis for any innovation concerning science students nowadays. So is our basis. As we turn our eyes towards the major concerns, we can see that war is not so much concerned with the land disputes but the energy of this era. As it is defined as the capability to perform, it means the more energy a state has; the more capable it is of leading the world. Pollution is another big issue to handle because the traditional energy source has brought too many threats to living beings and their environment. Science is now looking to control the adverse behavior of the source rather than by eliminating the threats concerned or looking for an alternative innovation. Some of the footprints towards the desired destiny can be traced like Carbon Capture, Bio fuels, Hydrogen Fuel Cells, Renewable energy, Electric Cars, Hydropower, DC batteries etc. Although these are several attempts to lessen the need of Fossil Fuels, but unfortunately these all together cannot depose the need of Fossil fuels to a great extent. Hope the pursuit of change will be fruitful and the endeavour will meet the sought determination.

In recent decades, lithium ion batteries have captured the energy market, ranging from small portable devices like portable MP3 players to updated electric vehicles, replacing the refillable gasoline tank with a rechargeable DC battery. However, it has failed even theoretically in terms of maximum energy density to meet the desired EVs propulsion. On the other hand, metal air batteries have profound and persuading high energy density, such that it can truly replace the gasoline tank both in terms of cost as well as mileage[1, 2].

The tendency of this research and study was based on the analysis of metal air batteries. Metal air batteries (a DC battery) are one of the old ideas but, at the same time, one of the most modern and fruitful seeming advancements towards the solution of concerned energy problems. It can replace the conventional Lead Acid and Lithium-ion batteries with its 52% higher energy density than LI-ion batteries with no harmful emissions and less weight, as the theoretical specific energy of Li-air batteries is 13,300Wh/kg for Li/O₂, whereas that is 100–250 Wh/kg for Li-ion batteries[3].

The problem with the launching was its limitation to being a primary battery. But now the problem seems to be solved by some of the leading field research companies as TESLA introduced the patent for the safe electric recharging of Lithium-Air batteries, which turned everyone's attention towards the option[4].

Aluminium is the most abundant metal in the earth's crust and also, because of its having appropriate properties, it is considered to be a highly attractive source of energy as the anode in a metal-air battery. The low atomic weight (28.98g/mol) and trivalent oxidation state of aluminium yield a low gram-equivalent weight (8.99) in addition to an ultrahigh specific gravimetric capacity (2.89Ah/g). Only lithium has an edge on aluminium in terms of slightly higher electrochemical equivalent value, i.e., 3.86 Ah/g. Li-air batteries have been mainly focused on the use of artificial feed of O_2 , to avoid moisture and other contaminants at the air cathode, while aluminium air batteries use ambient air[5].

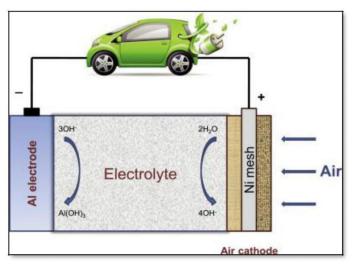


Figure-1: Schematic representation of Al-air battery

The **basic idea** of a metal air battery involves four parts, as shown in (Figure 1)

- Metal anode.
- Electrolyte.
- Separator / electrolyte absorber.
- Air cathode.

The separator is an insulator, which could only allow the transformation of ions. The electrochemical process yields energy and is the direct consequence of the following two types of reactions:

- Anode oxidation reaction, which means metal anode is dissolved in the electrolyte after the loss of electrons.
- Oxygen reduction reaction, which interprets the reduction of ambient oxygen or synthetic oxygen at air absorbing cathode.

Anode oxidation half reaction	$Al+3OH \rightarrow Al(OH)_3+3e^{-1.66V}$
Cathode reduction half reaction	$O_2+2H_2O+4e^- \rightarrow 4OH-+0.40V$
Overall reaction of the cell	$4A1 + 3O_2 + 6H_2O \rightarrow 4Al(OH)_3 + 0.71V$

Although there is some achievements made possible, regarding Zinc, Lithium, and Aluminium.

- Zinc was the first metal implemented in metal-air batteries[6].
- Zinc is stable in aqueous and alkaline electrolytes without significant corrosion.
- Commercial, primary Zn-air batteries have been used for many years to achieve long-term, low-rate discharge; it is the best alternative to low-capacity primary cells.
- MetAir Solstice –Personal Portable Power System/Emergency Preparedness the Zinc Air Battery Power was developed by Kevin Maloney, the founder, and is a very reliable emergency energy backup. It weighs 5 pounds and packs nearly 60,000 mAh, which is enough to charge up to 28 cell phones and can support a family of four at least for a week through its LEDs when the power is grid off. To use it, one has to remove the seal to let the air in for activating[7].
- The Zn air battery is limited because it is not rechargeable due to such reasons as dendrite formation, non-uniform zinc decomposition, limited solubility of the reaction products, and ZnO produced acts as an insulator.
- These are refulable, but with little complexion.
- Li is an extremely high specific energy anode material (3842 mAh g⁻¹for Lithium vs 815 mAh g⁻¹for Zinc)[8].
- Li-air cells are developed to be electrically rechargeable, a modern research area in Lithiumair batteries[9]
- Currently, Li-air batteries are still in the early development stage and their actual parameters fall far short of the theoretical values.
- Li-air cell capacity fades twice as fast after 50 cycles[10].
- Implementation of Li-metal anodes is associated with
- Dendrite formation.
- Electrolyte incompatibility (which results in resistive films forming on the anode surface).

The above problems can be troubleshooted by selecting an appropriate polymer electrolyte, which is,

- \checkmark Inert to Lithium metal.
- \checkmark It conducts Li-ions.
- ✓ It prevents dendrite formation.

In comparison to the lithium-ion battery, it has a higher energy density of 4302 WhKg-1, the potential for up to 8 times the range, and a significantly lower total weight[2].

Aluminum air batteries are yet to be used in day-to-day applications. However, the military has used this system as it is reliable and relatively lightweight. Phinergy is an Israeli company that develops aluminum-air energy systems. They state that batteries such as the aluminium air system can power various applications[11]. Although aluminium air batteries have not been developed for public use, there are many companies researching their use in consumer products as computer batteries, phone batteries, and backup memory batteries can not be recharged electrically but mechanically. Fuji Pigment Co. Ltd. has developed it with an appropriate weight

of 90 kg, covering 1700 km before recharge, that is with salt or fresh water. However, it also suffers from parasitic corrosion. However, Dr. Ryohei Mori addressed this problem by introducing ceramic and carbonaceous materials between aqueous electrolyte and electrodes as an internal layer[12, 13].

Advance mechanism: Illustrates both reactions as well as the advanced mechanism of mechanical recharging of an aluminium air battery (metal air battery) Figure 2. One can understand that there is an electrolyte tank which pumps the basic electrolyte to replenish the electrolyte and recycles the used electrolyte along with the impure contaminants. Professor Cho and his team developed a flow-based aluminum-air battery to continuously circulate the electrolytes, solving these issues. The battery and its electrolytes are also fire and explosion proof. According to UNIST (Ulsan National Institute of Science And Technology), this increased the discharge capacity of aluminum-air flow batteries by 17 times compared to conventional aluminum-air batteries[14].

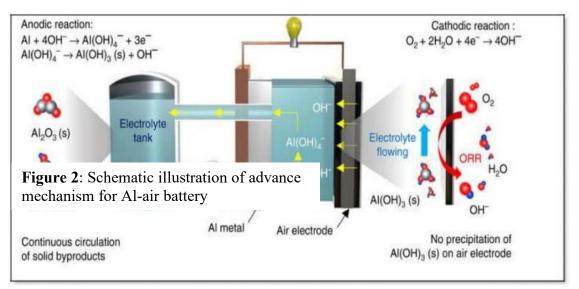


Figure 2: Schematic illustration of advance mechanism for Al-air battery

*Reason to select aluminium:*_Although we knew that on the top, the analysis was being done on lithium, silicon, cadmium, zinc, beryllium, and titanium, we preferred aluminium.

- To titanium, because aluminium was inexpensive[15].
- To beryllium, because beryllium is an extremely rare element[16].
- To zinc, because aluminium was easy to handle.
- To cadmium because aluminium is not toxic[17].
- To silicon because aluminium was easily available and inexpensive.
- To lithium because aluminium was not fire sensitive and was easy to handle on a laboratory scale[18].

The above mentioned priorities were limited to our experimental approach; otherwise, other elements had done theoretically well in terms of energy density. But these all had the flaws mentioned above.

Methodology

Using an open structure and more than 15 cells, the performance of an aluminum-air battery was evaluated. Aluminium was employed as the anode in conjunction with a variable assembly of

electrolytes, thickness of electrolyte absorber, ratio of MnO2 catalyst coated on the surface of activated carbon, and thickness of aluminium plate, and cell area. On the basis of the observation of experimental results in terms of Voltage and Current output, a graphical interpretation is created to illustrate the comparative outcomes of relative variation. Different amounts of NaOH and KOH were employed as basic electrolytes, while H2SO4 was used as an acidic electrolyte at the cathode and was separated from the NaOH electrolyte at the anode by a Polyethylene electrolyte absorber. Aluminum plates of 0.15mm and 0.30mm in thickness and 16in2 and 64in2 in area were utilised. In place of the specified cellulose, different thicknesses of tissue paper in terms of layers were utilised. MnO2 yielded ineffective results compared to other cell components, while it assisted in achieving the same outcomes with 20% less concentrated NaOH electrolyte. NaOH was chosen as the most cost-effective electrolyte since it is inexpensive and achieves the same function with a much lower concentration, hence extending the battery life.

Experimental analysis

In this investigation, three distinct concentrations of KOH, NaOH, and H2SO4 electrolyte were created. To activate the battery, 1.5 cc of electrolyte was put onto the absorbent pad (cellulose). The open circuit of the battery was recorded when the reaction region was completely saturated with electrolyte. The performance of the Aluminum-air battery was characterised by discharging the battery with a steady current. Varying discharge currents in the range of 10 mA to 50 mA were utilised to discharge the battery with various KOH/NaOH electrolyte contents. There were three repetitions of each test to get the mean value. All tests were performed at room temperature.

Results and Discussion

MnO2 was meant to increase the chemistry of activated carbon, however the opposite was true. Despite the fact that it decreased the output voltage of KOH, numerous combinations of other components were tested, but all studies revealed a steady voltage reduction or dormancy.

			ar	nd MnO2.			
Sr.no	cellulose	Activated	Aluminium	КОН	MnO ₂	Voltage	Current
	Layers.	Carbon.	plate			Output.	Output.
			Thickness.				
		(gm)	(mm)	(Mol)	(Ratio)	(volts)	(Ampere)
1.	4	25	0.15	3	0.125	1.38	0.8
2.	4	25	0.15	3	0.25	1.24	0.14
3.	4	25	0.15	3	0.5	1.44	0.67
4.	4	25	0.15	6	0.125	1.45	1.08
5.	4	25	0.15	6	0.25	1.53	0.38
6.	4	25	0.15	6	0.5	1.56	0.78
				NaOH			
				(Mol)			
7.	4	25	0.15	0.5	0.125	1.68	0.15
8.	4	25	0.15	0.5	0.25	1.7	0.12
9.	4	25	0.15	0.5	0.5	1.33	0.3
10.	4	25	0.15	0.5	1	1.69	0.13

Table 1: Chemical activity of the activated carbon on deferent Concentration and ratio of bases

Sr.	cellulose	Activated	Aluminium	КОН	MnO ₂	Voltage	Current
No.	Layers.	Carbon.	plate			Output.	Output.
			Thickness.				
		(gm)	(mm)	(Mol)	(Ratio)	(volts)	(Ampere)
1.	4	25	0.15	3	0	1.6	1.10
2.	4	25	0.15	4	0	1.41	1.3
3.	4	25	0.15	5	0	1.45	1.0
4.	4	25	0.15	6	0	1.54	1.28
5.	4	25	0.15	7	0	1.63	1.0
6.	4	25	0.15	8	0	1.51	1.0
7.	4	25	0.15	9	0	1.32	1.33
8.	4	25	0.15	10	0	1.53	1.10
				NaOH			
				(Mol)			
9.	4	25	0.15	0.5	0	1.60	0.3
10.	4	25	0.15	2	0	1.39	1.06
11.	4	25	0.15	2.5	0	1.64	0.92
12.	4	25	0.15	3	0	1.52	1.3
13.	4	25	0.15	4	0	1.60	1.18
14.	4	25	0.15	6	0	1.37	1.0
15.	4	25	0.15	10	0	1.45	0.93

 Table 2: Chemical activity of the activated carbon on deferent Concentration of bases without

 MnO2.

Table 3: KOH with different thickness of cellulose layers.

Sr.no	cellulose Layers.	Activated Carbon.	Aluminium plate	КОН	Voltage Output.	Current Output.
	Luyers.	Curbon.	Thickness.		Output.	ouipui.
		(gm)	(mm)	(Mol)	(volts)	(Ampere)
1.	4	25	0.15	7	1.47	1.0
2.	8	25	0.15	7	1.55	1.30
3.	12	25	0.15	7	1.60	1.66
4.	16	25	0.15	7	1.65	1.25
5.	20	25	0.15	7	1.64	1.12
6.	4	25	0.30	7	1.49	1.27
7.	8	25	0.30	7	1.45	1.13
8.	16	25	0.30	7	1.54	1.50

Table 4: Chemical activity of the activated carbon using NaOH and H2SO4 as electrolytes.

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Sr.	Nickel	cellulose	Activated	H2SO4	NaOH	MnO ₂	Voltage	Current
No.	Current	Layers.	Carbon.	(cathode	(anode		Output.	Output.
	Collector			electrolyte)	electrolyte)			
	(no of							
	Mesh							
	plates)		(gm)	(%)	(Mol)	Ratio	(volts)	(Ampere)
1.	Single	16	25	33.33	3	0	2.07	0.08
2.	Double	16	25	33.33	3	0	1.53	1.36
3.	Double	16	25	33.33	3	0.5	1.38	0.51
4.	Single	16	25	33.33	3	0.5	2.37	0.82

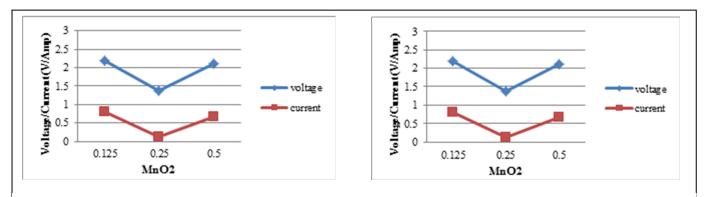
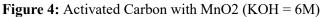
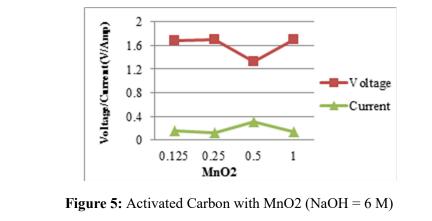


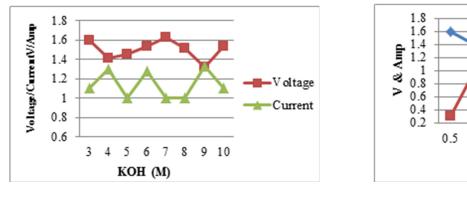
Figure 3: Activated Carbon with MnO2 (KOH = 3M)





According to the graphical representation in **Figure 3** and **4**, MnO₂ does not have any significant effect in terms of augmenting the voltage. But According to the graphical representation in **Figure 5**, MnO₂ showed some Effect in terms of augmenting the voltage at low concentration of NaOH.

In terms of increasing the amperes and volts, it would appear that MnO2 is of little use, as shown by the graphical depiction in **Figures 6** and **7**.



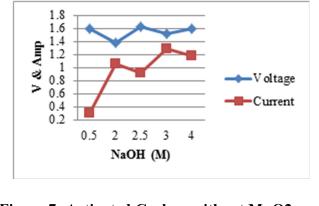


Figure 6: Activated Carbon without MnO2

Figure 7: Activated Carbon without MnO2

According to the graphical portrayal in **Figure 8** and **9**, employing a relatively thinner thickness results in higher voltage and amperage; however, this comes at the expense of a shorter lifespan for the cell. Additionally, the cellulose thickness should be at least comparable to 16 layers of tissue paper to be advantageous.

Table 5: Chemical activity of the activated carbon with different compositions of electrolyte mixtures and Areal variation.

Sr.no	KOH concentra tion. (Mol)	NaOH concentrat ion (Mol)	Potash alum.	NaCl. (Pure Salt)	Voltage Output. (volts)	Current Output. (Ampere)
Composition 1.	7	2.5			1.60	1.30
Composition 2.	7		Added		1.43	0.8
Composition 3.		2.5		Added	1.34	1.15
	1	Areal v	ariation			
		Area. (inch ²)	Activated Carbon. (gm)	Aluminium Plate thickness. (mm)		
Composition 4.	7	16	50	0.30	1.50	2.13
Composition 5.	7	32	25	0.30	1.51	1.63

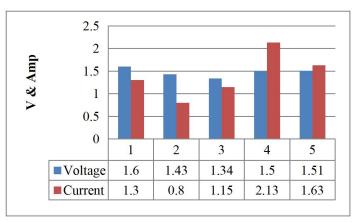


Figure 10: With different compositions of electrolyte mixtures.

As was said before, the pure 7 molar concentration produces the best voltage and amperes, as shown in **Figure 10**. However, even the composition that produced the best result among the first three seems to be irrelevant. On the other hand, expanding the surface area might be an option for achieving large amperes. If there is one thing that is crystal evident, it is that expanding the area will only be beneficial in terms of spewing out amps, and the same is true in terms of voltage when employing higher thickness.

Conclusion

The performance of an aluminium air battery with an open configuration was analysed, and the researchers came to the conclusion that the presence of MnO2 in an aluminium air battery while using a basic medium electrolyte was insignificant. They also came to the conclusion that the significance of NaOH over KOH in terms of low cost with lower concentration and comparable results was significant. When the activated carbon layer is made thicker, the ampere output decreases, while when the optimal surface area of the activated carbon granules is reduced, the ampere output increases. When measured in terms of voltage, the attempt to employ an acid and base composition as an electrolyte was successful, but when measured in terms of ampere, it was unsuccessful.

References

1. Li Y, Lu J. Metal–air batteries: will they be the future electrochemical energy storage device of choice? ACS Energy Letters. 2017; 2: 1370-1377.

2. Rahman MA, Wang X, Wen C. High energy density metal-air batteries: a review. Journal of the Electrochemical Society. 2013; 160: A1759.

3. Zhu AL, Wilkinson DP, Zhang X, et al. Zinc regeneration in rechargeable zinc-air fuel cells a review. Journal of Energy Storage. 2016; 8: 35-50.

4. Armand M, Tarascon J-M. Building better batteries. nature. 2008; 451: 652-657.

5. Mori R. Rechargeable aluminum–air battery using various air-cathode materials and suppression of byproducts formation on both anode and air cathode. ECS Transactions. 2017; 80: 377.

6. Oakes MJ. A brief history of batteries and stored energy. Neta World. 2006: 1-6.

7. Solstice M. Personal Portable Power System / Emergency Zinc Air Battery Power.

8. Kraytsberg A, Ein-Eli Y. Review on Li–air batteries—Opportunities, limitations and perspective. Journal of Power Sources. 2011; 196: 886-893.

9. Shao Y, Ding F, Xiao J, et al. Making Li-air batteries rechargeable: Material challenges. Advanced Functional Materials. 2013; 23: 987-1004.

10. Zhang T, Zhou H. A reversible long-life lithium-air battery in ambient air. Nature communications. 2013; 4: 1-7.

11. Mayer D. Phinergy offers aluminium as a new source of clean energy.

12. Mori R. Addition of ceramic barriers to aluminum-air batteries to suppress by-product formation on electrodes. Journal of The Electrochemical Society. 2014; 162: A288.

13. Fuji Pigment Co. L. Fuji Pigment Unveils Aluminium-Air Battery Rechargeable by Refilling Salty or Normal Water. 2015.

14. Foundation C. The 17X Aluminum-Air Battery.

15. Prasai B, Cai B, Underwood MK, et al. Properties of amorphous and crystalline titanium dioxide from first principles. Journal of materials science. 2012; 47: 7515-7521.

16. Kawamoto H. Japan's Policies to be adopted on Rare Metal Resources. NISTEP Science & Technology Foresight Center, 2008.

17. Coeurdassier M, De Vaufleury A, Badot P-M. Bioconcentration of cadmium and toxic effects on life-history traits of pond snails (Lymnaea palustris and Lymnaea stagnalis) in laboratory bioassays. Archives of Environmental Contamination and Toxicology. 2003; 45: 0102-0109.

18. Wang Q, Ping P, Zhao X, et al. Thermal runaway caused fire and explosion of lithium ion battery. Journal of power sources. 2012; 208: 210-224.