Abstract—Successful commercialization of zinc-air technology was first demonstrated in the 1930s when it was first used for railway signalling, since then much research has been done in this field. For applications such as remote telecommunication sites where extended backup power is necessary, zinc-air cells show great promise compared to the large battery banks currently used and expensive fuel cells under development. This paper explains what a zinc-air fuel cell is and what the implications are in the design thereof; it will also include results on the system designed. The paper will demonstrate the ability of the zinc-air fuel cell compared to a normal battery bank.

Index Terms—Zinc-air fuel cell, Batteries, Fuel Cell, Potassium Hydroxide, Gas Diffusion Electrode, polarization, Ohmic losses.

I. INTRODUCTION

The need for safe and environmentally friendly power has become one of the main topics around the world. Soaring oil prices and global warming has led to the development of these systems. The answer may be in fuel cells. Fuel cells are devices that convert chemical energy directly into electrical energy thus increasing the efficiency. These cells operate at efficiencies of 40 percent and up. One major disadvantage of most of these fuel cells is cost, due to the noble metal catalyst that is required. A promising alternative to more conventional fuel cells is the zinc-air fuel cell, which does not require any noble metal catalysts. Applications range from small electronic appliances to electric vehicles [1].

The zinc-air cell is an electrochemical device that converts chemical energy into electrical energy by means of an electrochemical reaction. The difference between conventional batteries and the zinc-air cell is that these cells get one of its main reactants, oxygen, from the outside air. This enables the zinc-air cell to theoretical reach specific energies of 1312 Wh.kg⁻¹, compared to 166 Wh.kg⁻¹ for conventional lead acid batteries [2]. Additional advantages over other battery technologies are that zinc-air cells contain no heavy metals and can operate over a wide range of temperatures. All this makes the zinc-air cell an attractive alternative power source for remote telecommunication sites.

There are three main types of zinc-air cells: primary cells, secondary cells and mechanically rechargeable cells. Primary cells are intended for single use and are then discarded after use. The secondary cell is returned to its original condition by forcing current in the opposite direction to discharge. In the mechanically rechargeable cell the anode and electrolyte are replaced when the cell is discharged, this replacement is continued until the life of the cathode is realised. A fourth kind of zinc air cell also exists and is termed the zinc-air fuel cell. The concept behind this cell is that unlike the previous three cells that have a limited amount of fuel inside the cell, the zinc-air fuel cell will have a constant supply of fresh fuel from an external tank.

The need for a fuel cell system aroused due to the energy requirements needed to power a 100 watt telecommunication system for one month. Using a zinc-air battery system consisting of 80 Ah cells would have required a battery bank of more than 1 000 cells. Through preliminary calculations it was shown that this figure could be greatly reduced when designing a fuel cell system. Due to this, the researcher attempted to design a smaller more economical fuel cell system instead of a huge battery bank which increases both cost and maintenance.

II. OPERATION

Electrical energy is generated when oxygen molecules from the atmosphere enter the gas diffusion electrode. Here the oxygen molecules split into individual oxygen atoms and water already present in the pores of the electrode reacts with the oxygen atoms to form hydroxyl ions. The hydroxyl ions migrate through the electrolyte and the physical separator to the zinc anode, where the hydroxyl ions bind to a zinc atom to produce zincate and two free electrons. The zincate immediately splits into two hydroxyls, one water and one zinc oxide molecule. The free electrons move from anode to cathode through an external load. Figure 1 shows a graphic representation of the reactions taking place on a molecular level.
III. CHEMISTRY

The electrical energy generated in the zinc-air cell takes place through two separate electrochemical half reactions at the individual electrodes.

\[
\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (1)
\]

\[
Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^- \quad (2)
\]

At the cathode (1), oxygen from the atmosphere enters the cell through an air-permeable, hydrophobic, catalytic membrane. Water already present in the pores of the membrane reacts with the oxygen to form hydroxyl ions. At the anode (2), oxidation takes place as zinc is converted to zinc-oxide by the reaction with the hydroxyl ions present in the electrolyte. The overall reaction that takes place at discharge is as follows:

\[
Zn + 2OH^- + \frac{1}{2} O_2 + \frac{1}{2} H_2O \rightarrow Zn(OH)_4^{2-} \quad (3)
\]

It is important to note that the electrolyte do not form part of the reaction, and only participates in the conduction of OH\(^-\) ions. The electrolyte used is a concentration of 28% by weight potassium hydroxide (KOH) mixed with distilled water.

IV. DEFINING THE ZINC-AIR FUEL CELL

Some confusion surrounds the terminology of a zinc-air cell. Many references refer to zinc-air technology as either a zinc-air battery, zinc-air fuel cell or when unsure, a zinc-air cell. One source suggests that a power source in which one of the active reactants is in the gaseous state, e.g. the oxygen in air, be termed a hybrid cell [3]. This raises the question: What is a zinc-air fuel cell and can it be classified as a fuel cell? To establish a clear definition for the zinc-air fuel cell there have to be look at other fuel cells and find the common factors that classify those cells as fuel cells.

A definition for the zinc-air fuel cell can be devised by looking at the two most popular fuel cells currently in development, they are: The Proton Exchange Membrane Fuel cell (PEMFC) and the Direct Methanol Fuel Cell (DMFC). The general factors between these cells are that they are electrochemical cells that convert chemical energy into electrical energy and use oxygen from the atmosphere as the oxidant. The obvious difference between PEMFC, DMFC and zinc-air cells is in fuel storage. Both the PEMFC and DMFC store their fuel external to the cell housing which only functions as an area for the reactions to take place. For this reason, a zinc-air cell can only be classified as zinc-air fuel cell when the zinc is stored outside the cell housing. The advantage of this is that unlike a battery, fuel cells can never “run flat” as long as there is a constant supply of fuel.

A zinc-air fuel cell can thus be defined as a device that electrochemically converts the chemical energy of a fuel and an oxidant to electrical energy. The fuel and oxidant are stored outside the cell and transferred into the cell as the reactants are consumed.

V. DESIGN

The biggest obstacle in developing a zinc-air fuel cell is in the design of an effective refuelling system. Due to the nature and phase in which zinc exist, some difficulties arise when designing a suitable refuelling process. The solid phase of zinc makes it almost impossible to circulate through the fuel cell stack as are done in both methanol and hydrogen fuel cells. Another problem in trying to design a circulating zinc-air fuel cell is that zinc is conductive; this means that even though the stack is made up of a number of cells, they will effectively be all connected to each other.

For the refuelling to be effective each cell should be refuelled individually from each other without the zinc being connected to each other. The objectives of the refuelling system were to have a mechanism that will introduce fresh dry zinc particles to the cell when required. The zinc will then pass through the cell were it will be discarded by the same mechanism used for refuelling. The mechanism is based on a rotational rod with a gap in it where the zinc particles can fall into. The rod is inside a block with gaps at both the top and bottom, the gaps is of the same width and length as that of the rod. The rod will rotate inside the block and eject the zinc particles into the cell with each rotation.
The same process is repeated at the bottom of the cell where the discharged zinc must be removed from the cell. Figure 2 shows a graphic of the components within the refuelling and removal mechanism that was used in the design of the zinc-air fuel cell. Rotation was achieved by connecting the gear to a chain which was driven by an electric motor. The electric motor and rod position is controlled and monitored by an electronic control unit.

Fig. 3. Gas diffusion electrode (GDE).

The design of the cell housing is based on that of a normal zinc-air battery. The cell design revolves around the GDE. The power capability of a zinc-air cell is directly proportional to the size or area of the GDE. The zinc-air fuel cell was designed using the electrically rechargeable zinc-air batteries that were supplied to the Vaal University of Technology for research purposes. These batteries have a prismatic shape with a dual GDE. The active area of one of these GDE’s is 9cm by 12cm giving a total active area of 108cm² for a single GDE. Employing a second GDE doubles the active area of a cell, increasing the power density of the cell. Figure 3 shows the GDE used in the design of the zinc-air fuel cell. A modification made to the existing cell was to add a metal grid to the centre of the cell. The grid acted as a current collector and conductor to the metal zinc particles. Due to the mobile electrolyte system, the cells also required additional electrolyte inlet and outlet. Figure shows a graphic of the cell.

Fig. 4. Zinc-air fuel cell.

Even though the title only states the design of a zinc-air fuel cell, additional equipment and design requirements are necessary for the fuel cell to operate successfully. Equipment such as external pumps and tanks for storage of both the zinc, discharged zinc and electrolyte are required as well as an electronic control unit for monitoring the potential of the stack and controlling the zinc feed to the cell when reaching a predetermined discharged voltage. Figure 5 shows a block diagram of the complete zinc-air fuel cell system.

Fig. 5. Complete zinc-air fuel cell system layout.

VI. RESULTS ON ZINC-AIR FUEL CELL

A. Voltage-current density

The voltage-current density characteristic curve of a single zinc-air fuel cell under test is given in figure 6. Vincent and Scrosati [3] explain that a typical cell polarization curve consists of three regions. The first region (A) undergoes a rapid fall in cell voltage at low current drains due to electrode polarization overvoltage (Defined as the voltage over and above the voltage predicted from standard tables of reduction potentials that must be applied before an electrochemical reaction occurs at the expected rate). In the second (B), almost linear region, the internal resistance of the cell components causes further voltage loss (iR polarization). In the third region (C), at relatively high current drains, the iR polarization is combined with further electrode polarization caused by the depletion of electroactive materials at the electrode surface. The three regions are indicated on the voltage-current curve of the zinc-air fuel cell in figure 6.

Fig. 6. Voltage-current curve of a zinc-air fuel cell.
Scott [4] explains that there are four loss mechanisms within a fuel cell, they are, reactant crossover and internal current losses, activation losses (A), ohmic losses (B), and gas diffusion losses (C). The losses within a zinc-air cell can now be better understand using the data and information Scott used to define the losses within a solid polymer electrolyte fuel cell.

Reactant crossover and internal current losses are to blame for the voltage loss between the thermodynamically expected voltage of 1.65 V and the open circuit voltage of about 1.4 V. There are two reasons for this: (i) While the electrolyte must be a good ion conductor within a zinc-air cell, it must be an excellent electron insulator. Since the electrolyte cannot be perfect, there will always be some trace of current flow through the electrolyte which will result in a voltage drop. (ii) There will also be some trace of reactant migration through the electrolyte producing useless heat. The theoretical open circuit voltage of the zinc-air fuel cell can be calculated by the following formula [5]:

$$E^0 = \frac{-1 \Delta G_f}{zF}$$

Where:
- \(E^0\) = Theoretical voltage of zinc-air fuel cell, V.
- \(\Delta G_f\) = Gibb’s free energy of elements in their molar form, KJmol\(^{-1}\).
- \(z\) = Number of electrons transferred in the external circuit.
- \(F\) = Faraday’s constant, 96485 C.

$$E^0 = \frac{-( -318.3 \times 10^{3} )}{2 \times 96485} KJmol^{-1}C^{-1}$$

$$E^0 = 1.65 V$$

Activation losses (region A; dominates the low current densities) occurs when the initial current begins to flow, there will be a steep decline in voltage drop before the curve flattens out. This is because electrochemical reactions naturally proceed rather slowly (particularly at the cathode), this requires the reactions to be “activated” by using an increase voltage drop to “pull” the charged particles across the electrode-electrolyte double layer interface. The voltage will usually fall to about 1.2 V, allowing the current to flow more rapidly.

Ohmic losses (region B; dominate the mid current densities) are losses that are connected with the current flow through the components of the power source. The ohmic losses originate in the electrolyte, the gas electrodes, the connection electrodes and any other material through which both electronic and ionic currents must flow inside the cell.

Gas diffusion losses (region C; dominate the high current densities) as well as the consumption of the solid electroactive material zinc, in the zinc-air cell, are responsible for the voltage loss in region 3. As the current increases there comes a point when the reactant gas and zinc electrode are being consumed at such a rate that starvation of the electrolyte-electrode interfaces occur. Usually, suffocation is most severe because the \(O_2\) is already diluted by the air’s \(N_2\). \(N_2\) is also responsible for reducing the rate at which \(O_2\) diffuses through the pores of the gas diffusion electrode, blocking the pores, thus preventing or slowing the diffusion of \(O_2\). At the anode, zinc is oxidized at such a rate that a barrier of zinc-oxide forms around the electrode, increasing the internal resistance and decreasing the area of the zinc. The point at which these constraints begin to limit efficiency is usually near the point of maximum power which will seldom be reached in practical operation of the cell.

### B. Power-current density

From the data recorded in the previous experiment, the power density curve can be determined. The power-current density curve was calculated by using the formula \(p(t) = v(t)\) times \(i(t)\). Figure 7 shows the result of the calculations. Maximum power capability at the point where the power curve reaches maximum curvature. Although capable of delivering the power, it is below the nominal operating voltage of the zinc-air fuel cell which falls between 1.2 V and 0.9 V. For maximum efficiency the cell should be operated at current densities less than 20 mA.cm\(^{-2}\). The downside is that the system will require additional cells to maintain power at low stack voltages.

![Power-current density curve](image)

### C. Influence of temperature on fuel cell

Cell voltages and current densities are higher at higher temperatures. This can be seen in figure 8 where there is a clear increase in performance with a increase in temperature. The major reason for the performance increase is that high temperatures increase the catalytic properties of the reactions taking place at the individual electrodes. Due to the mobile electrolyte system, the electrolyte can easily be heated external to the fuel cell stack, increasing the performance of the cell. But, performance increases with higher temperatures is however not practical due to the aqua’s nature of the electrolyte which will quickly evaporate. Other disadvantages when designing a system operating at these temperatures is the time it will take the system to reach the operating temperatures, increasing the initial start-up time of such a system.
Fig. 8. The effects of temperature on fuel cell.

A zinc-air fuel cell stack can reach operating temperatures of 40 °C and higher due to the reactions taking place within the cells. This usually happens at high discharge loads. Although there is an increase in stack temperature, the stack is protected against thermal runaway due to the limitation at which oxygen form the air gets consumed by the cell, thus limiting the current.

D. Mobile vs. static electrolyte system.

The mobile electrolyte system performed better than the static electrolyte system at high discharge rates as shown in figure 9. The reason is a constant supply of fresh ions in the mobile electrolyte system whereas the main reasons for the reduction in power within the static electrolyte design is due to ion depletion at the electrode surface which reduces the rate of the reaction at high discharges. Another reason is the layer of zinc-oxide (ZnO) that grows on the zinc granules at high discharge loads, reducing electrolyte diffusion to the undischarged zinc particles. An added advantage is that the zinc particles are continuously washed by the flow of re-circulating electrolyte. This circulation removes the reaction product, zincate, which prevents precipitation of the discharged products in the electrode active area.

Fig. 9. Mobile vs. static electrolyte system.

VII. CONCLUSION

Zinc-air fuel cells have the advantage of high energy density, good environmental compatibility, low cost of materials and wide operating temperature. The major advantage in the design of a fuel cell system compared to a battery bank of the same energy capacity was the reduction in the number of cells required. Through calculations and preliminary results it was shown that the battery bank will require about a 1 000 cells to power a 100 watt telecommunication site for one month were as the fuel cell system will only require about 50 cells. This all showed the importance of designing the fuel cell system. It was observed that a zinc-air fuel cell has the potential to power various applications. However, problems persisted in the refuelling process as well as constant leaking of the aqua’s electrolyte. Solutions to these problems were also explored within the research.

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REFERENCES


In 2004, Dewald began his full time studies as a Masters student at VUT in the field of Fuel Cell research under the support of Telkom COE.

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