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Design and Manufacturing of a Micro Zinc-Air Fuel Cell for Mobile Applications

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Abstract: Generating electrical energy for mobile applications requires specific characteristics including high energy density, high specific energy and low temperature. In this paper a Micro Zinc-Air Fuel Cell (MZAFC) has been constructed to provide the required electrical energy for small-scale vehicles. The manufactured cell provided a very smooth voltage-current characteristic curve which is very important for design purposes. The cell has been assembled and tested on a small vehicle.

Key words: Zinc-Air Fuel Cell (ZAFC) · Chem-E-Car competition

INTRODUCTION

The issue of global warming and the pollution of environment that is increasing due to fossil fuels and toxic metals in batteries have forced to search new sustainable energies which can replace old sources.

Also rapid development of portable electronic equipment and devices demands ever-increasing energy and power density. The fuel cell, a plausible next generation power generating system which is known to convert efficiently fuels to electricity with producing environmentally benign byproducts, is a potential candidate for alternative energy.

Among various types of fuel cells, Metal-Air Fuel Cells have attracted enormous attention as a possible alternative because of their various advantages (Table 1) such as high energy density, flat discharge voltage, low cost and abundance. Thus, some characteristics of Metal-Air Fuel Cell enable designers to design smaller, lighter and thinner devices. The electrochemical combination of a metal as an anode to an air electrode provides a cell with an endless cathode reactant and, in some cases, very high specific energy and energy density. The most famous type of cell in this category is the Zinc-Air Fuel Cell, though Al-Air and Mg-Air cells have been commercially produced [1-4]. Table 2 summarized the metals that have been considered for use in Metal-Air cells with several of their electrical characteristics.

Table 1: Properties of Metal-Air Fuel Cells

Advantage
High energy density
Flat discharge voltage
Long shelf life (dry storage)
No ecological problems
Low cost
Disadvantage
Drying-out limits shelf life once opened to air
Limited power output carbonation of alkaline electrolyte
Sluggish reaction of oxygen in cathode

Table 2: Candidate Metals for Metal-Air Fuel Cells

Metal anode	Mg	Al	Zn
Electrochemical equivalent of metal	2.20	2.98	0.82
Theoretical cell voltage (V)	3.1	2.7	1.6
Valence change	2	3	2
Theoretical specific energy	6.8	8.7	1.3
Practical operating voltage	1.2-1.4	1.1-1.4	1.0-1.2

One of the potential Metal-Air cells candidates, zinc has received the most attention because of it is the most electropositive metal which is relatively stable in aqueous and alkaline electrolytes. In all cases the basis of operation is the same. They are considered as a fuel cell

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because they can be 'refueled' by adding more metal to the anode and the cathode reaction is exactly the same as fuel cell [5, 6].

Some characteristics of MZAFC such as high specific energy, high power density, cheap and abundantly available fuel, no use of precious metals as catalysts and no issue of difficulty in fuel storage and transportation, has made it definitely one promising option for both stationary and mobile applications. Zn-Air cells are already in practice as a primary battery in small devices like hearing aids. MZAFC can replace alkaline or mercury batteries because its energy density is up to five times of these batteries. Recently, several companies are involved in development and commercialization of Zn-Air cells for electric vehicles, indoor power generators and industrial facilities. In addition to outstanding performance, Zn-Air technology boasts two additional features that make it extremely attractive:

Safety: A Zn-Air cell is an inherently safe battery, in storage, transportation, use and disposal. The danger of fire, explosion or personnel exposure to hazardous materials is lower than in any other battery technology.

Environment: Zn-Air cells contain no added mercury or other hazardous elements such as cadmium that are often used in batteries and in fact Zn-Air batteries can be disposed of with household trash.

Several approaches for Zn-Air cells have been proposed by different people and research groups. Since the first Zn-Air cell have constructed in 1932 by Heise and Schamacher the development of cathode and anode of the ZAFC began. In 1995 Cooper presented a new design of ZAFC which could discharge electricity continuously [7].

Remaining the byproducts within the cell and clogging, was the reason to make his ZAFC unpractical. In 2004, Pluto *et al.* [8] suggested an advanced architecture of ZAFC which solved the previous observed problems of ZAFCs. Recent efforts have focused on construction of high performance air diffusion cathodes. In 2010, Neburchilov *et al.* [9] have conducted a wide research on the construction of air diffusion cathode and the effect of various catalysts on the performance of the air cathode in ZAFC.

In the present study, to provide the required power and energy for driving a small-scale car (specifically for Chem-E-Car competitions), a MZAFC was constructed. The detailed description of the cell and cell stack is given as well as the result of the fuel cell operational test. Also the main problems of constructing these kinds of fuel cells are discussed.

Basis of Voltage Generation in a MZAFC: The MZAFC works on the basis of a reaction between the atmospheric oxygen and zinc in a liquid alkaline electrolyte. Since the MZAFC produces only zinc oxide; this is entirely recyclable without gas emission while generating electricity. Also the product is considered environmental friendly.

For generating electricity from a MZAFC, the overall reaction should be thermodynamically favorable. It is convenient to express the overall reaction in terms of the overall cell electromotive force, E_{emf} (V), which is defined as the potential difference between a cathode and an anode. The E_{emf} is related to the electrical work done in a cell.

$$W = -Q \times Eemf \tag{1}$$

where:

W is the electrical work done and Q is the transferred charge. The transferred charged is carried by the electrons; thus one can calculate it from:

$$Q = nF \tag{2}$$

where n is the number of electrons which take part in the chemical reaction and F is the Faraday constant. Therefore, the electrical work can be described as:

$$W = -nF \times Eemf \tag{3}$$

If there is no loss in the system, the electrical work done is equal to the Gibbs free energy change:

$$Eemf = \frac{\Delta Gr}{nF} \tag{4}$$

In the case of MZAFC, n=2 thus the equation becomes:

$$Eemf = \frac{\Delta Gr}{2F} \tag{5}$$

In MZAFC at the negative electrode zinc metal reacts with an alkaline electrolyte (usually potassium hydroxide) to form metal oxide, the released electrons pass through an external electric circuit to the air cathode where they are available for the reaction between water and oxygen to form hydroxide ions. Fig. 1 shows a general schematic diagram of a MZAFC.

The overall procedure during discharge can be described as the following electrochemical reactions of anode and cathode in alkaline solution, respectively:

Anode:

$$Zn \rightarrow Zn^{2+} + 2^{e-}$$

$$Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2-} \quad -\left(E^0 = 1.25V\right)$$

$$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^-$$

Cathode:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

($E^0 = 0.4$ V)

Overall Reaction:

$$2Zn + O_2 \rightarrow 2ZnO \quad (E^0 = +1.65 \text{ V})$$

In the above reactions, E^0 represents the standard electrode potential of each reaction with respect to the standard hydrogen electrode at the standard temperature and pressure. The overall cell electromotive force is calculated as:

$$Eemf = E^0 \text{ (cathode) - } E^0 \text{ (anode)} \qquad (6)$$

So that the overall cell electromotive force of a MZAFC should be theoretically 1.65 V. The $_{\text{Eemf}}$ is a thermodynamic value which does not include internal losses. The open circuit voltage (OCV) is obtained at no load condition and should theoretically be equal to the E_{emf}. However, the actual open circuit voltage of a practical MZAFC is always less than the theoretical value due to various potential [10].

MZAFC is composed of three major parts, zinc metal as an anode, an air electrode as a cathode and a separator. Each part of this structure has its own procedure to be constructed.

Construction

Required Materials: Copper mesh, Activated car-bon, Zinc powder, Cellulose paper, Potassium hydroxide, Ethanol and Cardboard.

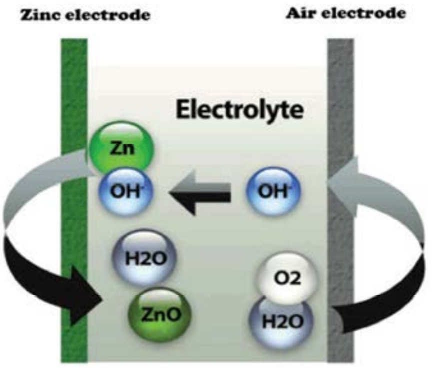


Fig. 1: Schematic of MZAFC

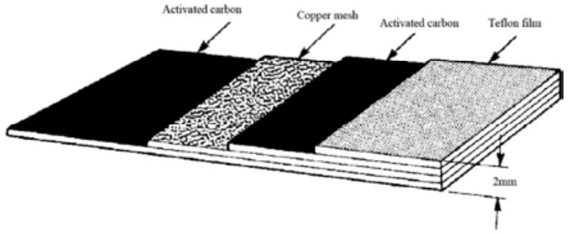
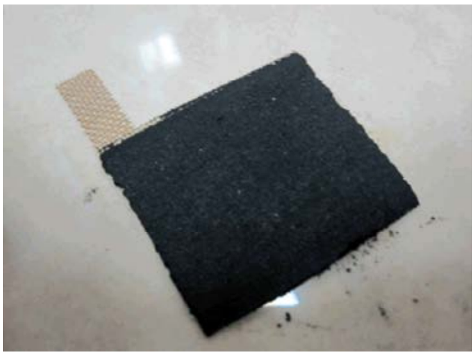


Fig. 2: Layers of a typical air cathode

The electrolyte used in present work is a 8M solution of potassium hydroxide. To prepare it 44.88 g of potassium hydroxide should be weighed and dissolved in 80 ml of deionized water. Since the solution process is exothermic, it is necessary to wait until it gets cold to 30°C. Then add water until the total volume reached to 100 ml.

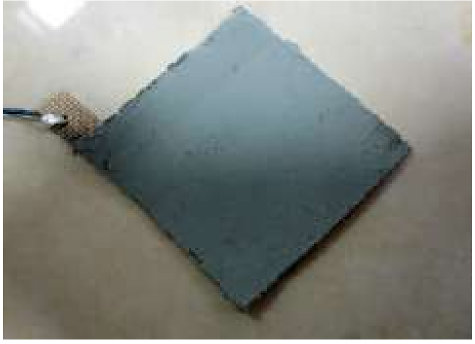
Construction of Air Electrode: Successful operation of a MZAFC is a strong function of an effective air electrode. The highly porous structure of air electrodes makes a diffusion path for oxygen. Therefore, carbon materials such as activated carbon can be used as substrates for the air electrode due to its high degree of micro porosity. Typically [11], an air electrode is composed of two active layers bounded to each side of a current collecting screen as shown in Fig. 2. An appropriated current collector should be firm enough and also made up of highly conductive substance. Copper mesh was the best choice because of its unique characteristic of being a firm and highly conductive metal. Among the procedures to embed the current collector within carbon layers the one with minimum destruction to the activated carbon porosity is the method of applying the mixture of ethanol and activated carbon on both sides of current collecting mesh. From another point of view, the carbon porosity increases electrolyte vaporization and this phenomenon caused changing the concentration of potassium hydroxide.

(a) Current collector



(b) Coated Cathode

Fig. 3: Constructed air cathode



(a) Without separator

(b) With separator

Fig. 4: Constructed zinc anode

Use of a thin film of Teflon on the outer side of the cathode which is in contact with air decreases the water transpiration. Hence a layer of Teflon was sprayed on one side of the cathode (Fig. 3). It should be considered that the air must have an unobstructed path through the device and into the cathode as a result the oxygen in the air is available to be discharged.

Construction of Zinc Electrode: MZAFC use pure zinc metal as an anode active metal. The most practical method of improving the performance of the zinc anode is to increase the surface area of the zinc particles, so that the zinc can react efficiently with electrolyte. Accordingly, the usage of zinc powder increases the reaction surface of zinc and electrolyte. The procedure of construction of the zinc electrode was the same as that have been performed for air electrode. Zinc powder and ethanol were mixed until a paste was formed then the paste was applied on the copper gauze which was cut in square shape as it is shown in Fig. 4a. After drying out the zinc plate was wrapped with separator paper (Fig. 4b). Thick separator prevents hydroxide ions to move properly and a thin separator might cause internal voltage loss because of internal short-cut.

Separator: The function of the separator in MZAFC is to transport the hydroxide ion, OH^- from the air electrode to the zinc electrode. The basic requirements of a proper separator are stability in alkaline solution, porosity and high ionic conductivity. A good choice for separator is cellulose paper [12, 13].

Assembling: The setup is quite simple except the unique air diffusion cathode which plays a decisive role in the whole construction process. It is well known that the kinetic of the oxygen reduction reaction is very sluggish [11, 14]. This phenomenon decreases power density and high rate discharge. On the other hand, this problem is a commonly observed one in cells using oxygen as active material, such as other metal air cells and fuel cells. Therefore, many efforts to overcome this problem have focused on finding proper way to improve the oxygen reduction reaction. One of the suggested ways to overcome the problem is to increase the cathode surface. Practically, this can be done by using two air diffusion cathodes at both sides of the zinc electrode as is schematically shown in Fig. 5.

The next stage was to construct a suitable cell holder which provides a clear path for air through the cell and a good compression between cell's layers (Figure 6).

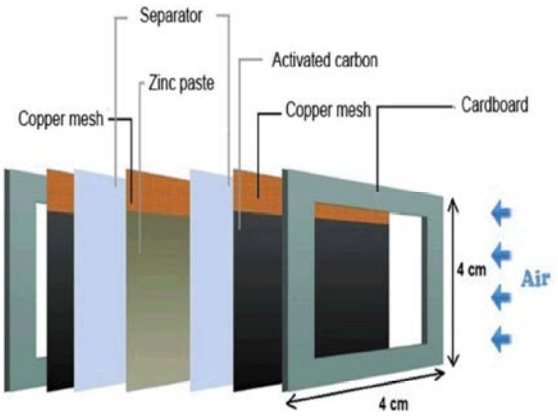


Fig. 5: Construction of MZAFC

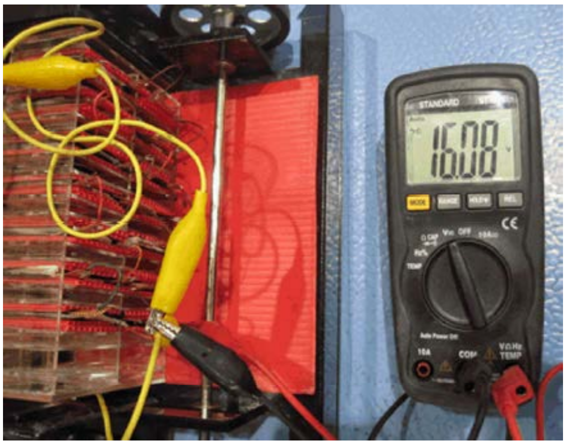
Fig. 6: Plexiglas MZAFC holder

Table 3: Electromotor Specifications

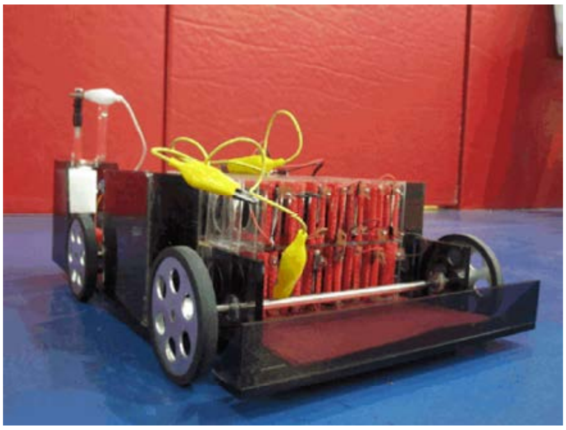
	No load		
Voltage (V)	Speed (rpm)	Current (mA)	
12	70	110	
	At maximum efficiency		
Gear ratio	Speed (rpm)	Current (mA)	Torque (Kg.cm)
1:78	60	240	1

The assembled MZAFC was put in a pan which contains 8M KOH so that the MZAFC layers could be soaked with electrolyte and MZAFC begins to work.

The output voltage of cell stack that consists of 14 cells was found to be16 V (Fig. 7a). The constructed MZAFC then connected to an electrical motor whose characteristics are listed in Table 3. This motor has enough power to derive a small scale vehicle as it can be seen in (Fig. 7b). Fig. 8 shows the variation of voltage and current across the electrical motor with respect to the time.



(a) Operational Voltage



(b) Final Assembly

Fig. 7: Assembled MZAFC on a smale-scale car

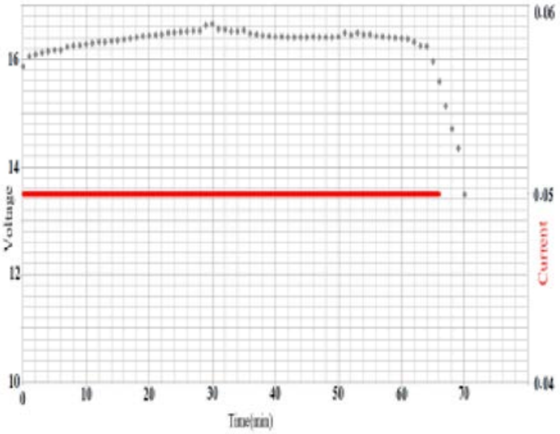


Fig. 8: Discharge curve for MZAFC

Factors Affecting the Performance of MZAFC: Even though the theoretically available voltage of a MZAFC is 1.65 V, the practically attainable value is always less than that due to the losses described below.

Ohmic Losses: Ohmic losses occur due to the electrical resistances of electrodes and interconnections and the resistance to the flow of ions in the electrolyte. The amount of voltage drop (V) depends on the current (i) and the resistances of components (R). This can be expressed as:

$$V=iR \tag{7}$$

The ohmic losses can be minimized by using the electrodes with high electrical conductivity and the electrolyte with high ionic conductivity.

Activation Losses: Activation losses result from the slowness of reactions taking place on the surface of the electrodes. In low-temperature fuel cells, the air cathode is primarily responsible for the activation loss. The activation loss increases as the current density increases. This loss can be reduced by increasing the active surface area of cathodes. Increasing the oxygen concentration by using pure O_2 instead of air can also reduce the activation loss, but this is not favorable because of the high cost of O_2 and the difficulty in oxygen compression and storage for small portable devices.

Carbon Dioxide Absorption: As the system is operated with air instead of pure oxygen, CO_2 present in the air dissolves in the electrolyte forming carbonate. The formation of carbonate increases the viscosity of the electrolyte and decreases its ionic conductivity. The problem of carbonate formation can possibly be reduced if an acidic electrolyte is adopted instead of an alkaline.

CONCLUSION

In this paper, construction of a MZAFC is presented. Beside the detailed information about the manufacturing of each part and the problem of sluggish performance of air cathode is fully discussed and a proper solution is given.

The constructed cell was assembled and tested on a small-scale vehicle and a good performance was achieved.

ACKNOWLEDGEMENTS

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Nomenclature:

Eemf	Overall cell electromotive force, V
W	Electrical work done
Q	Charge, C
E^0	Standard electrode potential, V
n	The number electrons that take part in chemical reaction
F	The faraday constant, $C.mol^{-1}$
ΔG	The Gibbs free energy change

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