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

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Abstract

Generating the 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.

Keywords

Zinc–Air Fuel Cell (ZAFC), Chem–E–Car competition

Nomenclature

E_{emf}	Overall cell electromotive force, V
W	Electrical work done
Q	Charge, C
E^0	Standard electrode potential, V
n	The numeber of electrons that take part in chemical reaction
F	The Faraday constant, C.mol^{-1}
ΔG_r	The Gibbs free energy change

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 efficiently convert 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 I) such as high energy density, flat discharge voltage, low cost and abundance, thus some characteristics of Metal–Air Fuel Cell enables 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. Table II lists the metals that have been considered for use in Metal–Air cells with several of their electrical characteristics. Of the potential Metal–Air cells candidates, zinc has received the most attention because 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 because they can be refueled by adding more metal to the anode, and the cathode reaction is exactly the same as for a fuel cell [1,2].

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, industrial facilities. In addition to outstanding performance, Zn–Air technology boasts two additional features that make it extremely attractive: [**?**, **?**, **?**, **?**, **?**, **?**, **?**, **?**, **?**, **?**, **?**]:

1. **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.
2. **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 [**?**]. Remaining the byproducts within the cell and clogging, was the reason to make his ZAFC unpractical. In 2004 Pluto et al suggested an advanced architecture of ZAFC which solved the observed problems of previous ZAFCs [**?**]. Recent efforts have focused on construction of high performance air diffusion cathodes. In 2010 Neburchilov et al 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, which is entirely recyclable, without gas emission while generating electricity, it is considered environmentally 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.

$$W = -Q \times \ E_{emf} \tag{1}$$

TABLE I: An example table.

Advantage
High energy density
Flat discharge voltage
Long shelf life (dry storage)
No ecological problems
Low cost (on metal use basis)
Capacity independent of load and temperature
Disadvantage
Drying-out limits shelf life once opened to air
Limited power output
Carbonation of alkaline electrolyte
Sluggish reaction of oxygen in cathode

TABLE II: Metal–Air candidate matals

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

where:

W is the electrical work done and Q is the tarnsfered charge. The transfered 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:

$$W = -nF \times \ E_{emf} \tag{3}$$

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

$$E_{emf} = \frac{\Delta G_r}{nF} \tag{4}$$

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

$$E_{emf} = \frac{\Delta G_r}{2F} \tag{5}$$

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.

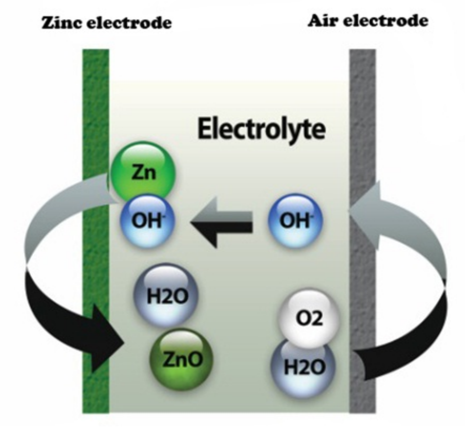


Fig. 1: Schematicn of MZAFC

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

- Anode:
  $Zn \longrightarrow Zn^{2+} + 2\,e^-$
  $Zn^{2+} + 4\,OH^- \longrightarrow Zn(OH)_4^{2-} \quad (E^0 = -1.25\ V)$
  $Zn(OH)_4^{2-} \longrightarrow ZnO + H_2O + 2\,OH^-$
- Cathode:
  $O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^- \ (E^0 = +0.4\ V)$
- Overall reaction:
  $2\,Zn + O_2 \longrightarrow 2\,ZnO \ (E^0 = +1.65\ V)$

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:

$$E_{emf} = E^0(\text{cathode}) - E^0(\text{anode}) \tag{6}$$

So that the overall cell electromotive force of a MZAFC should be theoretically 1.65 V. The E_{emf} 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 [3].

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 carbon, Zinc powder, Cellulose paper, Potassium hydroxide, Ethanol and Cardboard.

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

A. 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 [?], an air electrode is composed of two active layers bounded to each side of a current collecting screen as shown in figure **??**. 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 cause changing the concentration of potassium hydroxide.

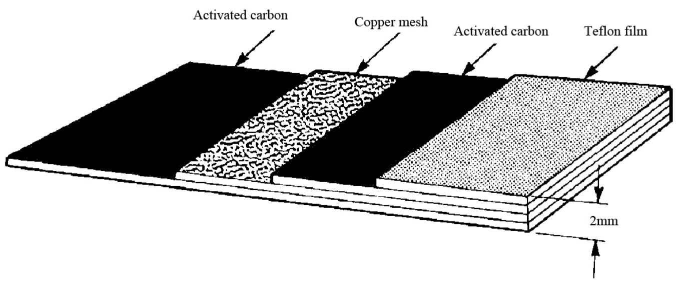
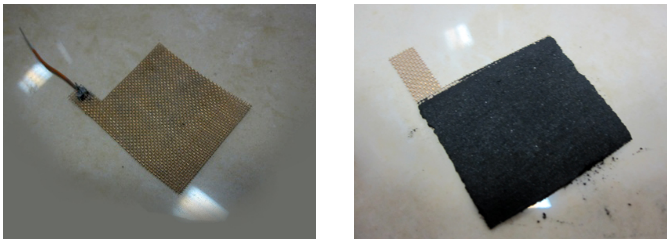


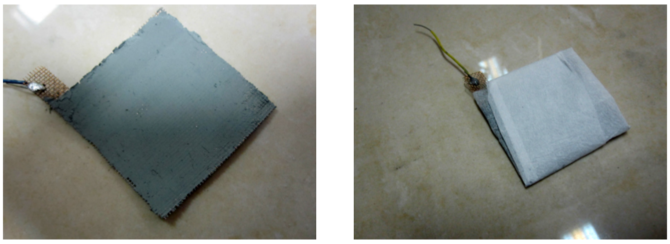
Fig. 2: Layers of a typical air cathode

Using a thin film of teflon on the outer side of the cathode that is in contact with air decreases the water transpiration. Hence a layer of teflon was sprayed on one side of the cathode (see figure **??**). 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.



(a) Current collector (b) Coated Catode

Fig. 3: Constructed air cathode



(a) without separator (b) with separator

Fig. 4: Constructed zinc anode

B. 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 can be seen if figure ??. After drying out the zinc plate was wrapped with separator paper (figure ??). Thick separator prevents hydroxide ions to move properly and a thin separator might causes internal voltage loss because of internal short–cut.

C. 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 [?, ?].

Assembling

The set-up 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 [?, ?]. This phenomenon

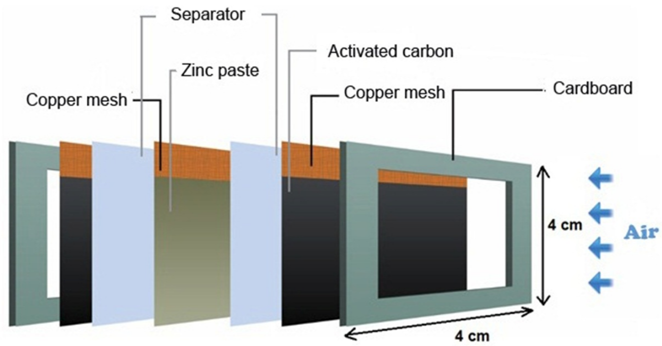


Fig. 5: Construction of MZAFC

TABLE III: Electromotor Specifications

Voltage (V)	No load		
	Speed (rpm)	Current (mA)	
12	70	110	

Gear ratio	At maximum efficiency		
	Speed (rpm)	Current (mA)	Torque (Kg.cm)
1:78	60	240	1

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 figure ??.

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 (see figure ??). The assembled MZAFC was put in a flat 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 (see figure ??). The constructed MZAFC then connected to an electrical motor whose characteristics are listed in Table ??. This motor has enough power to derive a samll–scale vechile as it can be seen in figure ??.

Figure ?? shows the variation of voltage and current across the electrical motor with respect to the time.

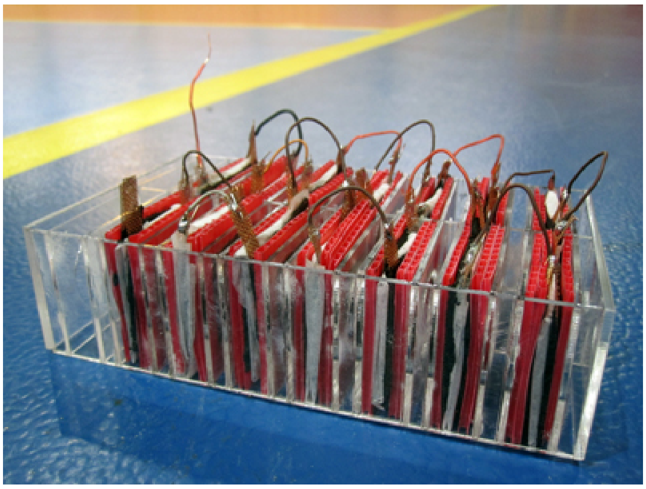


Fig. 6: Plexiglass MZAFC holder

(a) Operational Voltage (b) Final Assembly

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

MZAFC performance

In most cases of electrochemical devices, the performance is usually expressed in terms of polarization curve even though there are diverse types of methods and bases. Polarization occurs when the electrical resistance around the electrodes suddenly increases. In a typical polarization curve which can represent the performance of the cell or can indicate certain change in the cell, the voltage change is expressed in terms of the current change. The polarization curve exampled in Fig 9 is for a cell stack consists of four MZAFCs. This polarization curve can be divided in to three zones as follows:

1. Activation loss zone ranging from the OCV at zero current to the initial steep decrease of voltage.
2. Ohmic loss zone where the voltage slowly drops.
3. Concentration loss zone where the mass transport effect is dominant and the voltage rapidly falls at high current.

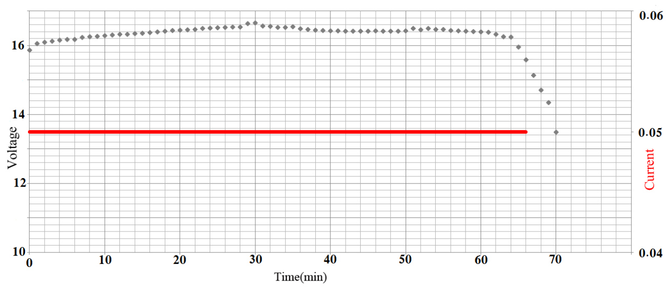


Fig. 8: Discharge curve for MZAFC

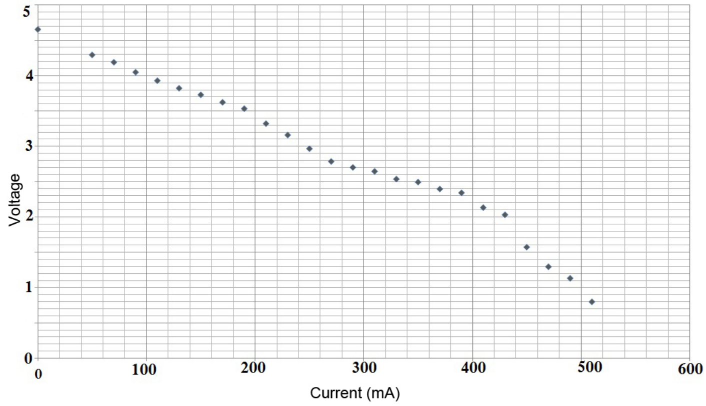


Fig. 9: Typical polarization curve of MZAFC

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.

A. 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.

B. 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.

C. 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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