Design and fabrication of a micro zinc/air battery

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Abstract: Micro-batteries are one of the key components that restrict the application of autonomous Microsystems. However little efforts were made to solve the problem. We have proposed a new planar zinc/air micro-battery, suitable for autonomous microsystem applications. The micro-battery has a layered structure of zinc electrode/alkaline electrolyte/air cathode. A 3D zinc electrode with a high density of posts was designed to obtain a high porosity, hence to offer a best performance. A model of the micro-battery is developed and the device performances were simulated and discussed. A four-mask process was developed to fabricate the prototype micro-batteries. The preliminary testing results showed the micro-batteries is able to deliver a maximum power up to 5 mW, and with an average power of 100 μW at a steady period for up to 2hrs. Fabrication process is still under optimization for further improvement.

1. Introduction

Rapid development of micro-electro-mechanical system and microelectronics makes miniaturization of systems possible. Microsystems with integrated sensors, actuators and control electronic circuits have been widely used in various areas such as automotive and microelectronics industrials, space exploration, biomedical research and healthcare. Huge demand and great applications require the development of further scale-down microsystems with remote sensing/control capability. One of the great constraints for the development of such micro-systems, which has been largely neglected so far, is the power supply [1]. It either contributes a considerable mass and volume to the system, or requires wires to connect the external macroscopic power supply. The disadvantages of external macroscopic power sources are obvious such as connecting problem, noise problem and less portability. These are particularly problematic for autonomous micro-systems for space exploration and implanted biomedical kits. With a proper on-board micro-power supply, the development of an autonomous micro-system in low weight and small volume without constraint of power wires becomes possible.

Zinc/air electrochemical system has been used for macro-batteries system owing to its high power density and energy density, excellent safety characteristics and low cost as compared to other electrochemical battery systems [2], as shown in Figure 1. In the last a couple of years, the electrochemistry of zinc air has been investigated extensively, and various types of zinc/air batteries have been developed for commercial purpose such as those used in hearing aids. However no attempt has been made to fabricate micro-batteries from zinc/air system. Here we propose a new planar structure zinc/air micro-battery, which is suitable for applications in micro-autonomous system. A mathematical model was developed using the MatLab program. The model is based on the
investigation of zinc/air battery with porous zinc electrode by Sunu et al.[3] and the extended research on the air electrode by Mao et al.[4]. The performance of the micro-batteries were simulated and optimized with the electrode porosity and electrolyte concentration as variables. Based on the modelling results, a four-mask process was then designed and developed to fabricate the micro-batteries. Here we report the preliminary fabrication and testing results.

![Figure 1. Comparison of energy density for different types of battery systems. Zinc air battery is one of the batteries that have the highest energy density per volume and per weight.](image)

2. Design and modeling

2.1 Design of the micro-battery

The planar structure of the proposed micro-battery is schematically illustrated in Figure 2. It is a cylindrical structure, consisting of a zinc bottom anode, a thin air cathode (Ni-mesh/carbon layers), electrolyte (KOH) between the electrodes, and two polymer walls with different height. The short one is called inner wall, and the tall one is called outer wall hereafter. An extension of Ni from the top electrode and seed layer of the bottom electrode form the leads to connect the loading for application.

![Figure 2. Schematic drawing of the proposed micro-battery.](image)

In order to increase the energy density and efficiency, high porosity zinc electrodes are normally used in batteries as they provide a high reaction area and better material usage. Instead of using the porous zinc film, a 3D zinc electrode with a high density of posts was used as the anode electrode in our
battery system. High-density post provides a large sidewall area for chemical reaction, hence improve the energy density. Also this technique has a better manufacturability and a better controllability of porosity by adjusting the height and density of the posts. The air cathode contains a hydrophobic Teflon layer, a thin Nickel mesh layer acting as a current collector and providing a structural support, and a carbon catalyst layer. Rather than using the standard gel electrolyte, KOH solution is used as the electrolyte to achieve the high energy density and efficiency as the concentration of solution can be much higher than that of the gel electrolyte. The inner wall is designed to support the top electrode and to provide a sealed housing for electrochemical reaction. The two-wall structure is to provide a practical construction with the ability to prevent corrosive electrolyte leaking out during the fabrication process and usage.

2.2 Chemistry

In the zinc/air system, the chemical reactions taking place are as follows [5]:

Anode:  \[ \text{Zn} + 4\text{OH}^- \Rightarrow \text{Zn(OH)}_4^{2-} + 2e^- \] (A)
\[ \text{Zn(OH)}_4^{2-} \Rightarrow \text{ZnO} + 2\text{OH}^- + \text{H}_2\text{O} \] (B)

Cathode:  \[ \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- \Rightarrow 2\text{OH}^- \] (C)

Overall:  \[ \text{Zn} + \frac{1}{2}\text{O}_2 \Rightarrow \text{ZnO} \]

Zinc/air battery not only provides a high energy density, but also has many advantages. Based on the electrochemical principle, it is clear that it produces electrochemical energy by using oxygen, which can be directly obtained from the atmosphere rather than from the system itself, which makes the miniaturization of micro-battery possible. The oxygen diffuses into the cathode during discharge and reacts with the electrolyte. The cathode acts as a catalyst to promote the reaction and it is not consumed at all. Therefore, it is possible to increase the energy capacity dramatically only by increasing the amount of zinc without increasing the overall size of the micro-battery significantly [6].

2.3 Modeling of the micro-battery

Based on the principle of electrochemistry of zinc in alkaline solution and the mass-transportation process in a battery, Sunu et al. have investigated the chemical reaction and charge transfer on a planar Zn electrode [3], Mao et al. [4] extended their investigation to the separator and the air electrode. We have combined and extended their models to the 3D-structure in a micro-dimension. In our model, the mass and charge conservation law, Ohm’s law in a liquid phase, current transfer in a solid phase (Buter-Volmer equation), the laws of the precipitation/dissolution rate and kinetic rate for zinc dissolution [7] were all considered. These are not discussed in detail here due to space limitation.

The micro-battery has a zinc base electrode with a footprint \(A\) and a thickness \(X\), and posts with a height \(h\). Since the post sidewall’s area is much larger \(A\), the chemical reactions and charge generation are dominated by those occurred on the sidewall surface. Therefore the energy density per area \(E/A\) is almost independent of the footprint of the anode electrode, but is strongly dependent on the post height \(h\) and density. Denser and higher zinc posts provide a high equivalent porosity. The porosity, \(e_0\) is defined as the ratio of empty spaces to whole volume of the anode. On the other hand, the rates of
chemical reactions are proportional to the hydroxide ion concentration $C_{o_0}$ in the electrolyte. Higher KOH concentration means higher reaction rates, and produces more power. Thus, the most important parameters to affect the performance of the batteries are the porosity of zinc electrode $e_0$ and the hydroxide ion concentration in electrolyte.

The energy delivering (or storage) capability and power capability are the most important factors for a micro-power source to be concerned for applications [1]. The simulation results showed that the energy delivering capability increases with increasing the zinc electrode thickness and reducing the output current density. However, from micro-autonomous application’s point of view, the micro-battery not only has a constraint in dimensions, but also has a specific power requirement. Thus the optimization objective is to maximize the energy output at a required current density for a micro-battery with the smallest dimensions.

![Figure 3](image3.png)

**Figure 3.** Simulated voltage output as a function of time and porosity at $C_{2o_0} = 8 \times 10^{-3}$ mol/cm$^3$, $I = 5$ mA.

![Figure 4](image4.png)

**Figure 4.** Simulated energy output as a function of porosity and KOH concentration at $I = 10$ mA.

Figure 3 represents the voltage output as a function of time with porosity of bottom electrode as variable. Figure 4 represents the dependence of the total energy output as a function of the porosity of the bottom electrode with KOH concentration as a variable. This figure is contour map with each line representing an equal energy output. The base zinc electrode thickness and the post height are 8 μm and 10 μm, and the spacing between the posts is 10 μm, respectively. Different porosities are achieved by adjusting the posts density. The total height of the micro-battery thickness is 100 μm, and the area is 1cm$^2$. It was found that the pattern of the energy output is similar for different current output. The optimal energy output lies in the upper right corner of Figure 4, where the electrolyte concentration is $\sim 20 \times 10^{-3}$ mol/cm$^3$ and the porosity of the zinc electrode is $\sim 90$ %. The max energy density however varies with varying the structural dimensions. Zinc powder is usually used to make the electrodes for commercial macro-zinc/air batteries, and it has a typical porosity of less than 70 %; also the gelled electrolyte used as a binder has an electrolyte concentration limitation. Both of the factors limit the performance of the macro-batteries. The newly proposed micro-battery however can have a much higher porosity and KOH concentration; hence it is superior in performance to the macro-counterparts.
A high porosity of zinc electrodes can be easily achieved using the microfabrication technology developed for microelectronics industrial.

3. Fabrication
A four-mask process has been developed to fabricate the micro-battery. The process flow is shown in Figure 5. A chromium/copper (5/10 nm) seed layer was firstly sputtered on a silicon wafer, and then was patterned by a standard photolithography. Zinc electrode was formed by two-step Zn-electroplating in a zinc-chloride solution at room temperature using positive photo resist (AZ4562) as a plating mould. Firstly the zinc posts were plated using the through-mask plating technique, and the zinc base was then plated. The Zn base thickness is typically ~10 \( \mu m \), and the post height is 15~20 \( \mu m \). SU8 negative resist was used to formed the inner and outer walls. The inner wall with a height of 60 \( \mu m \) was firstly made, and then the outer wall was formed on the outside with a height of 100 \( \mu m \) by photolithography to provide a better and stronger sealing. The electrolyte was then introduced into the inner chamber and the air cathode was put on the top of the inner wall as shown in Figure 2, and was sealed with optical-sensitive polymer.

![Process flow of micro-battery fabrication.](image)

Since the top air electrode has a very large area, it may bend and contact the bottom electrode, leading to the short-circuit. To prevent this, four SU8 posts were introduced in the middle of the bottom electrode to support the air electrode layer. The posts have a footprint of 100x100 \( \mu m \) and a height same as the inner wall. Figure 6 is the optical photo of a micro-battery made without the top electrode. The middle four large structures are the SU8 supports.

![Optical photo of micro-battery without air electrode.](image)

4. Results and discussion
Since the process is still to be optimized, the fabricated micro-batteries do not have the best performance. We only show the preliminary test results for discussion. A constant loading (100 Ohms) was used to test the micro-battery. Figure 7 shows the output current as a function of time. The micro-battery has a footprint of 1cm², a zinc base thickness of 10 \( \mu m \), zinc post height of 8 \( \mu m \) and a porosity of 20 \%. The electrolyte concentration was \( 8 \times 10^{-3} \) mol/cm³. The output current drops
drastically from 7 to 2 mA within a few minutes, and then decreases slowly with time to less than 1 mA for nearly 2 hours. This corresponds to an initial power output of ~5 mW, then down to ~0.1 mW at the steady state. The average output power in the steady period is roughly ~90 μW, which is too small for most autonomous applications, but sufficient for some specific applications such as RF remote control. The energy delivered during this period is about 0.5 Joule, roughly in agreement with the simulated results. However its output current is only tenth of that expected, and the output voltage drops too quickly. It was also found that the open circuit voltage of the battery without connecting to a load drops rapidly from 1.2 to 0.7 V within several hours. Leakage of the solution is believed to be responsible for the low open voltage measured due to poor sealing of the micro-batteries (electrolyte leaks and vaporizes). The small output current is mainly restricted by the low porosity of the zinc electrode used in these prototype devices. A high output current and a steady output voltage can be achieved once the battery has a high porosity and better sealing. Fabrication processes are to be optimized, and further testing results will be reported at the conference.

5. Summary
A micro zinc/air battery as an on-board micro-power source for autonomous micro-systems has been designed, modeled, and fabricated. Although the fabrication process needs to be optimized, the initial test results of the micro-batteries show that structure design and computer modeling are satisfactory, and the concept of this micro zinc/air battery is feasible for autonomous microsystem applications.

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