Printable on-chip micro battery for disposal bio-sensing device

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Abstract. This paper reports an on-chip micro battery which can be fabricated on a CMOS chip. The battery consists of screen-printed Mg and AgCl films. An open circuit voltage of 1.58 V, the maximum power of 1.4 mW and a total stored energy of 400 mJ were obtained from anode and cathode electrodes of about $3 \times 3 \text{ mm}^2$. Demonstration devices self-powered by the on-chip battery worked in a 0.14 M NaCl solution, and digital data transmission from the devices using optical and electrical field methods were confirmed.

1. Introduction
A disposal bio-sensing device is expected to be used in a point of care testing system such as rapid disease inspection in developing countries and home health care system. In these systems, inspection cost should be as small as possible. For this purpose, a disposal bio-sensing chip was proposed [1], in which recycling cost can be minimized. In this system, a small sensor chip without post-process was used to make the chip cost low. However, the on-chip micro coil for power feed and data transfer limits the miniaturization, i.e. the cost reduction was limited. Therefore, in this paper, we proposed an on-chip micro battery which can be printed on the sensor chip. To simplify the system, a single cell battery should generate sufficient voltage for a CMOS chip. We chose Mg as an anode material and AgCl as a cathode material. A chip size can be reduced due to high power density of the battery, which reduces the chip cost. In addition, wireless communication method implemented in the chip does not require any electric wirings connected to the chip, which drastically reduces the post-process cost.

2. Disposal bio-sensor chip
Figure 1 shows the schematic of a disposal bio-sensor chip using an on-chip battery. The Hall sensor array and signal processor are fabricated by a standard CMOS process. Antibodies specifically bind to the inspection target (antigen) are fixed on the sensor array. A on-chip battery consists of Mg and AgCl films is placed on a CMOS chip. Bio-sensing is usually done in an aqueous solution such as saline, which can be also used for an electrolyte of the battery with some salt. This technique enables long-term storage and simple structure. Two types of wireless communication methods are proposed to transfer the inspection result: optical and electric field methods. The optical communication type device (Dig. 1(a)) transfers the digital data using light emission or color change. For this purpose, LEDs, organic ELs or electrochromic devices are fabricated on the chip. The electric field
communication type device (Fig. 1(b)) induces the electric potential distribution in the electrolyte which can be sensed by external pick-up electrodes.

Figure 2 shows the inspection procedure. First, the sensor chip is immersed in an inspection solution, then the test sample (urine, blood etc.) are introduced. If the test sample contains an inspection target (antigen), the targets are fixed on the sensor chip by antigen-antibody coupling. Then micro beads made of magnetic material combined with antibodies which also specifically bind to the target antigen are introduced. Thus, the magnetic beads are fixed on the chip again using antigen-antibody coupling. If the magnetic beads exist on the sensor ship, the perpendicular magnetic field is induced by the applied magnetic field parallel to the surface, which can be detected by the hall sensors. The sensor chip is activated by adding salt such as NaCl or NH₄Cl to the solution, then it counts the number of magnetic beads and send the result by optical or electrical methods.

3. Printable on-chip micro battery

3.1. Fabrication procedure
Several methods for deposition of the Mg film such as vacuum evaporation [2] and electroplating [3] were already reported. However, these methods take long time for thick film deposition. Therefore, in this paper, we proposed a printing method to deposit thick films for both Mg and AgCl electrodes. Figure 3 shows the fabrication process of the printable battery. First, current collection electrodes made of Cu were fabricated on the device. A stencil mask made of 250 μm polypropylene paper was prepared by a cutting plotter, and aligned to the Cu pattern. An Ag/AgCl paste (ALS Co., Ltd) was then screen-printed on the Cu electrode. The thickness of the printed paste can be controlled by that of stencil mask. After removing the mask and drying the paste at room temperature, another stencil mask was aligned and a Mg paste, which was prepared by mixing 0.05 g of Mg powder (Wako Pure Chemical Industries, Ltd) with 0.06 g of Ag dispersed conductive epoxy resin (Chemtronics), was printed and cured at 70°C. Finally, unnecessary area was covered by an UV curable resin. Figure 4 shows the schematic of the test sample. The area of both electrodes was 3 × 3 mm².

3.2. Performance of on-chip micro battery
The fabricated test battery was evaluated by a setup as shown in Fig. 4(b). 0.14 M NaCl solution was used as the electrolyte. Various load resistors were connected to the battery and the applied voltage was measured by a digital multimeter (34410A, Agilent Technologies Inc.). Figure 5 shows the
measured performance of the battery. The open circuit voltage, the internal resistance and the maximum output power were 1.58 V, 520 Ω and 1.4 mW, respectively.

Figure 3. Fabrication procedure.  Figure 4. (a) Structure of the test device and (b) measurement equipment.

Figure 6 shows the time dependency of the output voltage using the 3.3 kΩ load resistor. The output voltage was stable as long as about 650 s and the total energy obtained by the battery was as high as 400 mJ, which is sufficient for the disposal application.

Figure 5. Output performance of the on-chip battery.  Figure 6. Long time operation and generated total energy.

Figure 7 and 8 show the scanning electron micrograph (SEM) and energy dispersive X-ray spectrum (EDS) of the anode and cathode electrodes, respectively. Before power generation, the Mg particles on the anode electrode were covered by Ag particles which came from the conductive epoxy resin (Fig. 7(a) and 8(a)), and the cathode electrode was covered by Ag and AgCl (Fig. 7(b) and 8(b)). After power generation, Mg was eroded and cracks and voids were formed, and the Ag particles on the Mg were partly removed (Fig. 7(c)). From the EDS analysis, the atom ratio between Mg and O was about 29:71 (Fig. 8(c)), which implies not only main reaction

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^- \]

but also side reaction

\[ \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg}(	ext{OH})_2 + \text{H}_2 \]
occurred. In fact, the gas formation on the anode was clearly observed. On the other hand, cathode was covered by pure Ag (Fig. 8(d)), which means almost all of AgCl was reduced to Ag as

$$\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-.$$  

**Figure 7.** SEM of (a) anode and (b) cathode before power generation, and (c) anode and (c) cathode after power generation.

**Figure 8.** EDS of (a) anode and (b) cathode before power generation, and (c) anode and (c) cathode after power generation.

4. Demonstration device

A CMOS chip requires both long time and high cost for development. Therefore, in this paper, we used commercially available CMOS device combined with the developed on-chip battery to confirm the operation of the system. Two types of demonstration devices were fabricated and tested: optical and electric field data communication types.

Figure 9 shows the schematics of these demonstration devices. A microprocessor (PIC12LF1501, Microchip Technology Inc.) was used as the CMOS device. LEDs and communication electrodes were used for optical and electric field data transfer, respectively. A printed circuit board (PCB) was used as a base board and these devices were soldered on it. The developed on-chip battery was printed on the backside of the PCB. Unnecessarily area was covered by the transparent UV-curable resin. The PCB size was about $5 \times 7$ mm$^2$.

Figure 10 shows the operation result of the optical type demonstration device powered by the on-chip battery in 0.14 M NaCl solution. Two LEDs were used as clock and data signals. On and Off of each LED could be clearly observed by a standard CMOS camera, and the digital data could be decoded.

Figure 11 shows the experimental setup for the the electric field communication through the electrolyte. Two pick up electrodes were inserted in the solution about 2 mm away from each communication electrode on the device. Figure 12(a) is the applied potential to the communication electrode, which was directly measured by a standard probe with an external power supply. Before the valid data, start bits with digital data of “101010” was sent to determine the baud rate and the start timing. Figure 12(b) shows the received signal using pick up electrodes. Due to a high pass filter formed by electric double layer, the measured signal showed positive and negative sharp peaks at rising and falling edges of the sending digital data. After passing through the digital filter, the digital signal was restored as shown in Fig. 12(c). The sampling timing was determined by the start bits, then the digital data was successfully decoded.
5. Summary
A printable on-chip battery for a disposal bio-sensor chip was developed and evaluated. The open circuit voltage of 1.58 V, maximum power of 1.4 mW and total stored energy of 400 mJ were obtained using 3 × 3 mm² electrodes. Demonstration devices using commercially available CMOS device were developed and the digital data was successfully transferred by optical and electrical methods. The proposed printable on-chip battery can be easily fabricated on any devices including CMOS chips at low cost. It is good candidate for the disposal bio-sensor as well as an ingestion sensor.

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