

# LASER-ASSISTED FABRICATION OF ELECTROCHEMICAL CELLS ON WAX PAPER

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**Abstract:** Functionality of paper based diagnostic devices can be enhanced by integrating them with a power source. Here we demonstrate fabrication of paper based electrochemical cells on wax paper using CO<sub>2</sub> laser surface treatment and micromachining. A four cell battery shows a steady output voltage of about 3 V. The battery can provide 0.25 mA for at least 30 minutes when connected to a 10 K $\Omega$  load. Higher voltages and more current can be achieved by adjusting the number and size of electrochemical cells in the battery without changing the fabrication process. Finally, an LED is powered using paper-battery to demonstrate its applicability.

**Keywords:** Point-of-care, Paper, battery, electrochemical cell, laser

## INTRODUCTION

Recently, there has been a growing interest in low-cost paper-based platforms for various applications including sensing [1–4], electronics [5], and actuation [6]. Point-of-care (POC) medical diagnostics is in particular a very attractive application area for paper-device-technology mainly due to lower costs and disposability as compared to plastic or glass based alternatives. These devices, being fabricated mostly outside a clean room, can play an important role in developing countries where cost and ease of operation are two main requirements (along with sensitivity and selectivity) [7]. Colorimetric paper devices [8,9] have shown a great potential in satisfying these criteria. However, their functionality is limited to visual inspections due to lack of a power source. Use of standard alkaline batteries not only increases the device cost but it also makes it difficult to dispose the device. A battery-on-paper can act as a stepping stone towards a self-powered, low-cost, disposable diagnostic device.

Among several approaches investigated for on-paper energy storage, one can mention carbon-nanotube (CNT) embedded paper supercapacitor [10]. However, the high cost of CNT prevents such approaches for low-cost applications. Paper based batteries have also been reported in the literature [11,12]. More recently, a multi-layer self-energized paper-based microfluidic device [13] that powers an ultraviolet LED was reported that uses built-in galvanic cells. The device, however, requires complicated fabrication process and multilayer assembly. Here, we report on a simple method to fabricate a paper-based battery through laser-assisted patterning of metals and hydrogel on a hydrophobic (wax) paper.

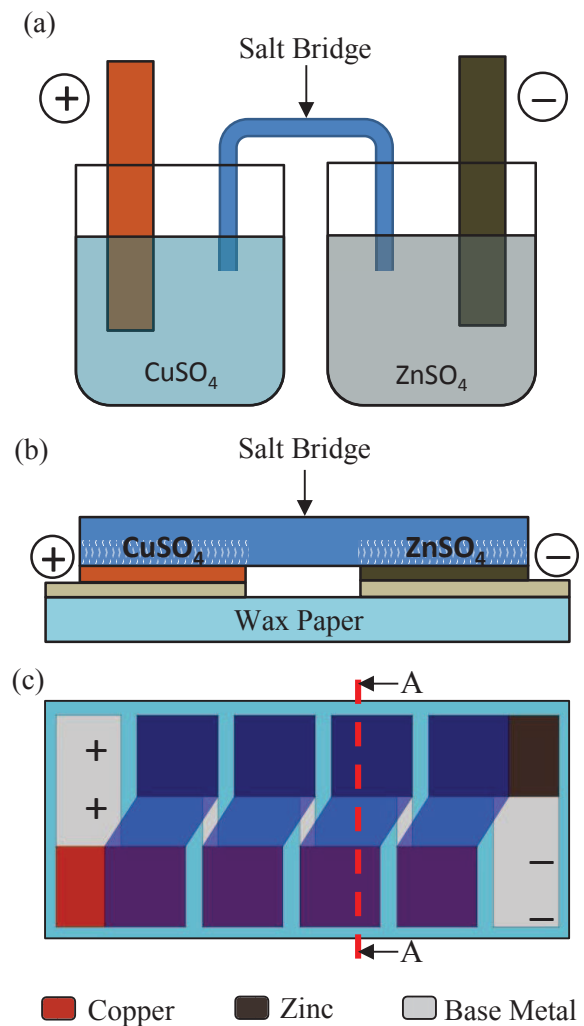


Fig. 1: (a) Basic electrochemical cell (b) design of electrochemical cell on paper (c) top view of paper battery showing 4 cells in series (Note: fig. (b) shows the cross-section A-A from fig. (c))

## EXPERIMENTAL

### Design

An electrochemical cell consists of two different metal/metal ion half cells connected by a salt bridge (Fig. 1-a). Difference in electrode potential results in a voltage across the metal electrodes. To achieve desired terminal voltage, multiple cells can be connected in series. Figure 1-b shows the schematic cross-section of the paper battery where the components of an electrochemical cell are transferred onto a wax paper. The device consists of a base metal layer coated with desired metals. Metal salts are present in the hydrogel at the corresponding sides to create metal/metal ion half cells. The hydrogel layer on top of these metals acts a salt bridge to connect these half cells. Figure 1c depicts the top view of the paper battery, where four cells are connected in series to achieve a higher output voltage. It is important to note that since all the metal patterns are presents on the same layer, creating multi-cell battery does not increase the fabrication efforts. There are various half cell combinations available which can be used in the paper battery. Copper and zinc was chosen for easy availability of these metals and corresponding electrolytes. Further, this cell provides a theoretical potential of 1.1 V which is a sufficiently large starting point.

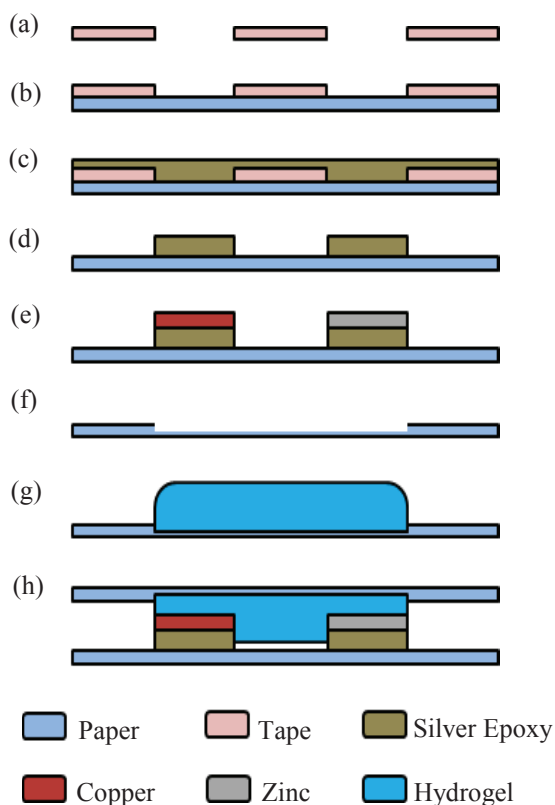


Fig. 2: Fabrication process of the paper battery.

With point-of-care diagnostic devices in mind, we restricted the size of the paper battery to  $(20 \times 50 \text{ mm}^2)$ . One can increase the size to allow more material and hence higher capacity. Based on the application, size and shape can be adjusted to meet the specific requirements.

### Fabrication

For our device, we used silver epoxy as the base-metal on top of which copper and zinc were electroplated. Fabrication process starts with laser cutting an adhesive tape (3M magic tape) using CO<sub>2</sub> laser (Universal laser systems, max. power 60 W, max. rastering speed 2 mm/ms) to create a screen printing mask (Fig. 2a). 50% of power at maximum rastering speed was sufficient to cut through the tape. This mask was temporarily bonded to wax paper (Fig. 2b). Silver epoxy (Creative Materials Inc., Part No. 118-09) was spun (5000 rpm, 60 s) to create a uniform thin layer (Fig. 2c). The adhesive tape was then peeled off to leave desired conductive patterns on wax paper (Fig. 2d). The adhesive tape (magic tape 3M) was chosen such that it bonds temporarily to enable masking but peels off easily without damaging the surface. After curing silver epoxy, copper and zinc were electroplated on corresponding electrodes (Fig. 2e). Next, a polyacrylamide-based hydrogel was patterned on a separate wax paper to be used as the

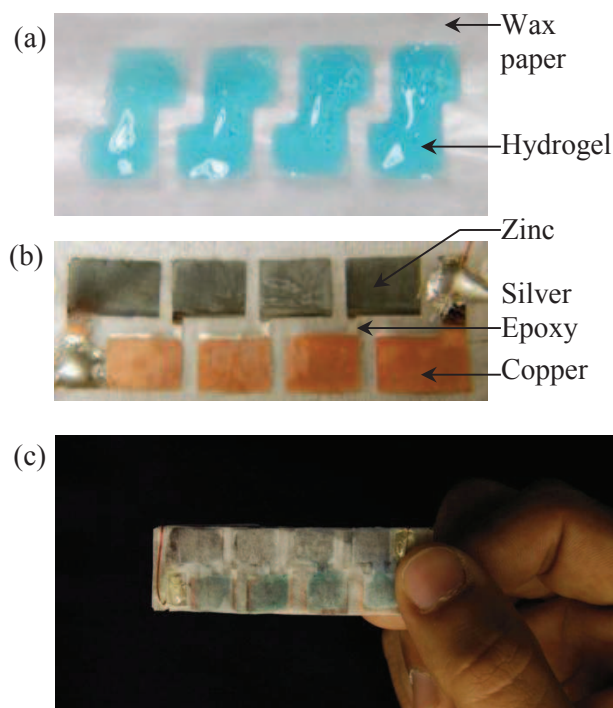


Fig. 3: (a) Hydrogel patterned on the wax paper (color added for visibility) (b) Metal patterned on the wax paper (c) final fabricated paper-battery.

salt bridge (Fig. 2f-g).

We used our previously reported laser surface treatment method [14] to create hydrophilic areas onto which the hydrogel was immobilized when the sample was dipped in hydrogel-precursor. Patterned hydrogel was soaked in potassium chloride solution to introduce the electrolyte. Finally, hydrogel layer was aligned and bonded on top of metal layer (Fig. 2h). Metal salts (copper sulfate, zinc sulfate) were sprinkled on corresponding electrodes before assembly. When hydrogel comes in contact with the electrode, salt dissolves in the water trapped inside gel-matrix. Figure 3 shows photographs of metallic pattern, gel pattern, and the final fabricated device with four cells. Long term storage can be achieved by drying the hydrogel after assembly (the battery can be activated by dipping it in water when needed).

### Measurements

Voltage across battery terminals was measured using a multimeter. To estimate the current capacity of the battery, various loads ( $R=0.1\text{ k}\Omega, 1\text{ k}\Omega, 10\text{ k}\Omega$ ) were connected to the battery and voltage drop across them was measured.

## RESULTS AND DISCUSSION

Figure 4 shows the characteristic curves of the paper battery. Figure 4a shows voltage obtained by using different (1-4) number of cells in series. On average,  $0.78\text{ V}_{OC}/\text{per-unit}$  was achieved which is lower than the theoretical value of  $1.1\text{ V}_{OC}/\text{per-unit}$ . This loss of external voltage can be attributed to migration of copper ions through the salt bridge. Although majority of copper ions are present near the copper electrode, some ions diffuse to zinc electrode and deposit on that electrode. This unwanted copper deposition at zinc electrode generates a voltage drop in opposing direction leading to reduction in overall voltage. Hence, immediately after assembly, when copper ions are not present at zinc electrode we observe  $3.8\text{ V}$  OC-voltage, and after about five minutes, a sharp drop to  $3\text{ V}$  is observed indicating initiation of opposing reaction (Fig. 4b). Once the reaction reaches equilibrium voltage stays steady at  $3\text{ V}$  for at least half an hour. Impurities in these chemical cells can also contribute towards the voltage loss.

When a  $100\ \Omega$  load is connected across the terminals, initially the battery provides up to  $2.2\text{ mA}$  current which drops to  $0.35\text{ mA}$  in 30 minutes (Fig. 4c). Higher loads lead to lower currents as expected. One can observe that a  $10\text{ k}\Omega$  load provides a stable current of about  $250\ \mu\text{A}$  (power =  $625\ \mu\text{W}$ ). This is

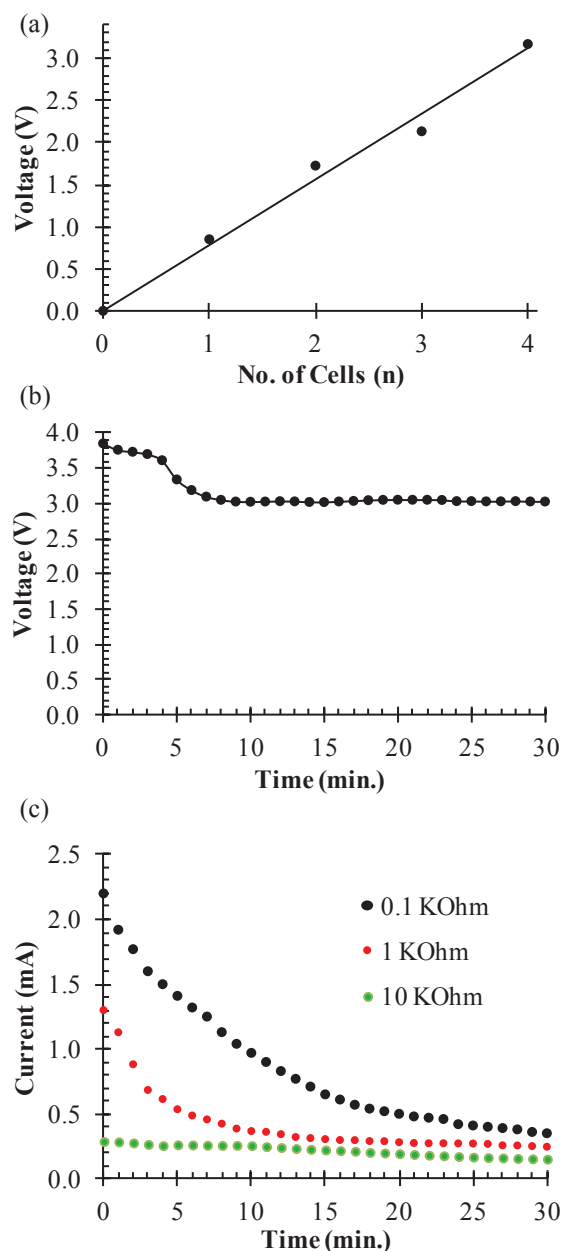


Fig. 4: (a) Voltage vs. number of cells (b) open circuit voltage vs. time (c) current through various loads for a four cell battery vs. time.

due to the fact that current provided by the battery is directly proportional to the number of charged carriers which depends on the rate of reaction. Since contact area between electrolyte and metal is limited, this puts a ceiling on the reaction rate. One can increase the output by increasing the contact area; however,  $625\ \mu\text{W}$  is adequate to power many diagnostic microdevices. Figure 5 shows a red light-emitting diode (LED) powered using paper battery.

Another important advantage of paper battery is its flexibility. It consists of thin metal layers, thin wax paper, and compliant hydrogel leading to small

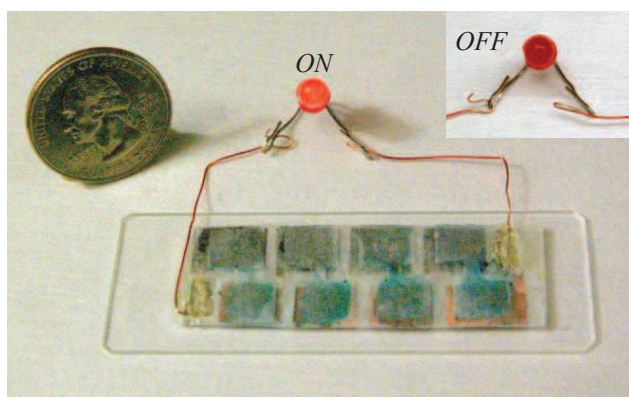


Fig. 5: A paper battery powering an LED (inset shows LED in off state for comparison)

bending stiffness of the assembly. One can wrap it around a cylinder or stick it on top of a wavy surface without losing its functionality.

## CONCLUSIONS

We successfully created paper-battery through patterning of metals and hydrogel on wax paper using CO<sub>2</sub> laser. A steady output voltage of ~3 V was achieved using a four cell battery. This battery provided ~0.25 mA for at least 30 minutes when a 10 KΩ load was connected. This power (625 μW) is sufficient for many sensing microsystems. For demonstration, an LED was lit using the paper battery. If desired, higher voltages and more current can be achieved by adjusting the number and size of electrochemical cells in the battery. The fabrication process is designed in such a way that it does not need extra effort to make such changes.

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