Journal of Power Sources 318 (2016) 163–169

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

A microfluidic galvanic cell on a single layer of paper

Krutarth H. Purohit [a], Saina Emrani [a], Sandra Rodriguez [a], Shi-Shen Liaw [a], Linda Pham [a], Vicente Galvan [b], Kryls Domalaon [b], Frank A. Gomez [b], John L. Haan [a], *

[a] *California State University, Fullerton, 800 N State College Blvd, Fullerton, CA 92834, United States*
[b] *California State University, Los Angeles, 5151 State University Drive, Los Angeles, CA 90032, United States*

HIGHLIGHTS

- Single layer of paper used to produce electrochemical power.
- Galvanic cell produces significant power on single layer paper.
- Hybrid galvanic and fuel cell produces the best power on paper.

ARTICLE INFO

Article history:
Received 27 January 2016
Received in revised form
30 March 2016
Accepted 31 March 2016
Available online 12 April 2016

Keywords:
Paper microfluidics
Microfluidic fuel cell
Electrochemical sensor
Point-of-care (POC) diagnostic devices
Environmental sensor

ABSTRACT

Paper microfluidics is used to produce single layer galvanic and hybrid cells to produce energy that could power paper-based analytical sensors. When two aqueous streams are absorbed onto paper to establish co-laminar flow, the streams stay in contact with each other with limited mixing. The interface at which mixing occurs acts as a charge-transfer region, eliminating the need for a salt bridge. We designed a Cu–Zn galvanic cell that powers an LED when two are placed in series. We also used more powerful redox couples (formate and silver, formate and permanganate) to produce higher power density (18 and 3.1 mW mg^{-1} Pd). These power densities are greater than previously reported paper microfluidic fuel cells using formate or methanol. The single layer design is much more simplified than previous reports of multi-layer galvanic cells on paper.

1. Introduction

1.1. *Paper microfluidic sensors*

The scope of microfluidic sensors encompasses biology, chemistry, agriculture, and medicine, due to their portability and efficiency [1]. They are particularly useful in applications that involve small quantities of available analyte or limited financial resources. Over the past decade, microfluidic sensor technology has spread to microfluidic paper-based analytical devices (μPADs) [2–11]. On these devices, the sensor is patterned on paper that is able to wick aqueous fluids, inducing laminar flow without the requirement of external pumping. Such devices can also be miniaturized to conduct multiple analyses in a small area while only requiring a small amount of analyte [12–17]. Many of these devices are designed for colorimetric sensing, which is used for both chemical and biological analysis. While colorimetric detection is very specific/selective for a desired analysis, this specificity makes development of a more universal sensor challenging [18]. The use of electrochemical sensing provides an avenue for broader-based sensor technology, where multiple analytes can be detected on a single device using amperometry [19,20].

1.2. *On-board power supplies*

The use of an electrochemical sensor naturally requires the provision of electrical power to drive the electrochemical reaction(s) of interest. Electrical power can also be used to power the readout that identifies and/or quantifies the analyte(s) present. Typically this power is provided by a disposable battery; often this battery will contain much more power than necessary for a single analysis and will leach excessive quantities of corrosive or toxic materials into the environment upon disposal. Therefore, it would be advantageous to the development of μPADs if paper-based power supplies are

---

* Corresponding author.
E-mail address: jhaan@fullerton.edu (J.L. Haan).

http://dx.doi.org/10.1016/j.jpowsour.2016.03.109
0378-7753/

developed that can be fully integrated with the analysis and be printed with only the necessary quantity of energy-containing materials for the analysis. In 2012, Liu et al., demonstrated an integrated battery and glucose detector for artificial urine analysis [18]. In the same year, Thom, et al., demonstrated an on-chip fluorescence assay powered by microfluidic galvanic cells [21]. Several layers of paper-based material were required in the construction of the integrated battery (five layers) and galvanic cell (20 layers). This integrated power is preferable to technology that requires a potentiostat or other external (and complex) electrical device, but the vertical layers create design complexity and opportunities for numerous resistive losses within the device [19,20,22,23].

1.3. Galvanic cells and fuel cells on paper

In addition to the aforementioned examples of integrated power supplies, numerous reports have been made that demonstrate power produced on paper microfluidic devices with the *potential* for integration into an operating electrochemical sensor. Paper microfluidic power devices have been demonstrated primarily in two forms: galvanic cells on paper and fuel cells on paper.

Galvanic cells on paper have been demonstrated in which the galvanic cell is comprised of all components common to laboratory-scale galvanic cells: two solutions, two metal electrode strips, and a salt bridge [18,21,24–28]. In a typical arrangement, the two solutions are separated from each other by different layers of paper since the solutions cannot be permitted to mix. The two metal electrode strips are connected to the paper via conducting tape or some other similar adhesion. Finally, the salt bridge is required to maintain charge neutrality in the separate solutions, so this bridge necessarily spans several layers of paper. Such designs are very promising since they produce a scaled-down version of the power that is possible through a galvanic cell, and a variety of metal redox reactions can be considered to produce the desired quantity of voltage, current, or power. However, these designs are very complex since they incorporate several layers in order to separate different components of the galvanic cell.

In 2014, Esquivel et al., demonstrated the first paper fuel cell that could potentially be used to power an integrated sensor. This fuel cell consisted of methanol fuel oxidized on Pt–Ru catalyst on Au support, and oxygen reduced in KOH on Pt catalyst [29]. In 2015, Copenhaver et al., demonstrated a paper fuel cell utilizing formate as fuel and hydrogen peroxide as oxidant [29]. The anode consisted of high surface area Pd, and the cathode was colloidal graphite paint. The main component of both fuel cell designs is a single strip of paper, much like that used for a paper-based analytical measurement. The advantage of this single strip is that the paper will induce co-laminar flow (through capillary action), keeping the anode and cathode streams separate. These separate streams behave similarly to a microfluidic fuel cell that does not require a membrane separator. In the Esquivel et al., design, the anode and cathode materials were not directly integrated into this paper, so multi-layer adhesion was required, but the electrode materials were directly painted onto the paper in the design by Copenhaver et al. Therefore, the direct-painted design represents an important step toward decreasing the complexity of a paper-based power supply by reducing the design to two dimensions.

In this work we demonstrate that a paper galvanic cell can be created using the same design principles of the paper fuel cells based on co-laminar flow. A hybrid of the fuel cell and galvanic cell electrochemistry can be used to design a superior paper-based power supply.

2. Experimental

2.1. Device fabrication

The device was fabricated on Whatman 3 filter paper cut to channel length of 4.5 cm and channel width of 1.8 cm. The channel width of each component of the galvanic/fuel cell was 0.9 cm. The device contained additional Y-shaped feeder channels to transport the reactants from reactant vials to the desired location on the paper device. In the process of transport, the reactants followed a co-laminar flow regime over the entire 4.5 cm length, resulting in two separate 0.9 cm channels of reactants with less than 1 mm of mixing.

The electrodes consisted of four small (4 mm diameter) dots painted directly on the paper using a commercial nail-dotting tool. The electrode ink was made using metal or carbon mixed with AS-4 ionomer (Tokuyama) and water. The loadings were as follows: 0.03 mg Pd per dot (10 wt% Pd/C, Fisher), 1.2 mg carbon per dot (colloidal graphite, Ted Pella), 1.2 mg Cu metal (carbon supported, synthesized in house via metal salt reduction) or Zn metal (powder, Aldrich).

2.2. Device testing

A continuous reactant flow condition was induced by capillary action in the paper, and the spent reactants were absorbed onto an absorbent pad connected to the top of the channel. A stopped flow condition was established by removal of the paper feeder channels from the reactant vials once the entire channel was soaked with reactants.

Several variations of reactants and electrodes were studied. The reactants included: aqueous solutions made from solid $CuSO_4$, $ZnSO_4$, and $AgNO_3$ (Fisher); HCOOK (Alfa Aesar).

Measurements of the electrochemical behavior of the galvanic/hybrid cells were taken using a Princeton Applied Research 263A potentiostat operating with two electrodes. Constant current measurements were taken at 1 mA under both continuous- and stopped-flow conditions. Voltage-current (VI) measurements were taken from open circuit to 10 mV in 20 mV steps at 2 s intervals. All VI measurements were taken under continuous flow conditions. A flat brass clip was used with a brass alligator clip in order to provide a strong connection between the painted paper electrodes and the potentiostat.

3. Results and discussion

3.1. Design concept

Previously, a microfluidic fuel cell (MFC) was designed in which reactants (potassium formate and hydrogen peroxide) flowed in a co-laminar fashion along a piece of filter paper. Due to the co-laminar flow, there is only a small region of reagent mixing and no reagent crosses over to the opposite electrode. At the Pd/C **anode**, the formate is electrochemically oxidized [30]:

$$\mathrm{COOH^- + 3\ OH^- \rightarrow CO_3^{2-} + 2H_2O + 2\ e^-}\ E^0{}_{anode} = -1.05\ \mathrm{V} \quad (1)$$

At the colloidal graphite **cathode**, the hydrogen peroxide is electrochemically reduced:

$$\mathrm{HO_2^- + 2\ e^- + H_2O \rightarrow 3\ OH^-}\ E^0{}_{cathode} = 0.88\ \mathrm{V} \quad (2)$$

Thus, the overall theoretical cell potential is 1.93 V. In this microfluidic fuel cell, the hydroxide flows from **cathode** to **anode** across the interface between the two reagents. In a standard fuel