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Electrochemical detection in paper-based analytical devices using microwire electrodes

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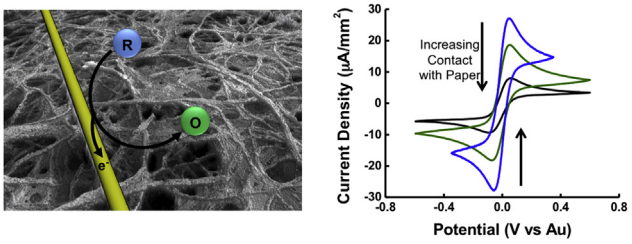
GRAPHICAL ABSTRACT



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ABSTRACT

Microwire electrodes are presented as an alternative to screen-printed electrodes for detection in electrochemical paper-based analytical devices (ePADs). Compared to carbon ink electrodes, microwire electrodes offer lower resistance and a significant increase in current density relative to carbon ink electrodes. Various microwire compositions and diameters, including 30 μm Pt, 25 μm Au, 18 μm Pt with 8% W, and 15 μm Pt with 20% Ir, were tested and compared to theoretically predicted behavior. The measured current in static solution was below predicted levels for cylindrical microelectrodes but greater than levels predicted for hemi-cylindrical electrodes most likely as a result of the proximity of the electrode to the paper surface. Furthermore, the current response was indicative of semi-thin layer behavior, likely due to the confined solution volume in the paper. After electrode characterization, a device was developed for the non-enzymatic detection of glucose, fructose, and sucrose using a Cu electrode in alkaline solution. The limits of detection for glucose, fructose, and sucrose were 270 nM, 340 nM, and 430 nM, respectively, which are significantly below sugar concentrations found in sweetened beverages or glucose levels in serum.

1. Introduction

Microfluidic paper-based analytical devices (μPADs) have become an area of interest since the first published multiplexed diagnostic detection using photoresist-patterned paper as a substrate material [1]. Most μPAD research has focused on providing simple, easy to use, inexpensive, and rapid measurements for point-of-care (POC) diagnostics and environmental monitoring [2–4]. Original μPADs used common filter paper that is inherently

Abbreviations: ePADs, electrochemical paper-based analytical devices; μPADs, microfluidic paper-based analytical devices; POC, point-of-care; PDMS, polydimethylsiloxane; SAM, self-assembled monolayer; CV, cyclic voltammetry; DPV, differential pulse voltammetry; HFCS, high fructose corn syrup.

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inexpensive, renewable, easy to modify, disposable, and consists of a hydrophilic capillary network capable of transporting fluid without external pumps [5–7]. To control flow direction and maintain analyte concentration, hydrophobic barriers were created using wax printing [8,9], photolithography [1,10,11], or printing of hydrophobic polymers such as polystyrene [12–14]. A wide range of detection methods have also been used with μPADs, including colorimetric, electrochemical, fluorescence, chemiluminescence and electrochemiluminescence [2]. Colorimetric detection is most common due to its simple reactions, ease of visualization and semi-quantitative results. However, electrochemistry has also been used due to its fast sensor response, lower detection limits relative to colorimetric methods, quantitative results, and ability for external electronics to be miniaturized [15,16].

Fabrication of electrochemical paper-based analytical devices (ePADs) has relied heavily on the use of carbon inks [2,10]. Carbon electrodes are typically fabricated by screen-printing or stenciling pastes or inks and the carbon material can be modified before electrode fabrication [10,17]. Using stencil-printing for example, microelectrodes with a chemical mediator have been fabricated for ePAD detection [17]. Metallic ink and sputter-coated electrodes have also been used, albeit to a lesser extent [10,18,19]. However, sputter-coated electrodes require expensive fabrication equipment and thus are not preferred when trying to keep device cost low. The most printed metallic ink is silver, and has been used primarily for reference electrodes [10,20]. Screen-printed gold ink has also been used as a working electrode material [21,22]. While inks and pastes are attractive and will continue to be used, they suffer from higher resistance due to the presence of polymer binders. The high electrode resistance and low electrode active surface area have led to the use of large electrode surface areas [23].

Recently, Crooks and coworkers fabricated ePADs with cylindrical microwire electrodes [24] using a similar concept to that reported by Garcia et al. for polydimethylsiloxane (PDMS) microfluidic devices [25]. Microwires have many advantageous characteristics including high conductivity, ease of modification, and availability in many different pure and alloyed compositions. They can also be cleaned and modified prior to incorporation using chemicals and solutions that cannot be used with ink, paste, or sputter-coated electrodes without contaminating or destroying the ePADs. The ePAD fabricated by Crooks et al., for example, used piranha solution (mixture of hydrogen peroxide and sulfuric acid) and subsequently modified electrodes with a self-assembled monolayer (SAM) prior to incorporation into the device [24]. Another advantage of incorporating an electrode with a micron-scale dimension is enhanced mass transport due to radial diffusion, leading to increased current density that should provide improved sensitivities and detection limits [26,27].

Although an ePAD device with microwires has been developed and studied for hollow and cellulose filled channels [24], a direct comparison of an ePAD made with carbon ink electrodes and microwires has not been reported nor has demonstration of alternative electrode materials. Here we report a direct comparison with carbon electrodes, demonstrating that microwire electrodes provide an improved current density. Electrode performance was studied using different compositions and diameters of microwires and comparing the results to established theory for cylindrical and hemicylindrical electrodes. Measured current density at varying cylinder radii followed theoretically predicted trends, but the paper acted to decrease electroactive area. As an example of the utility of this approach, a microwire ePAD device with a Cu electrode was developed for the non-enzymatic electrochemical detection of the carbohydrates glucose, fructose, and sucrose in a variety of beverage samples [28–30]. Good agreement was found between the method and a commercial glucose assay.

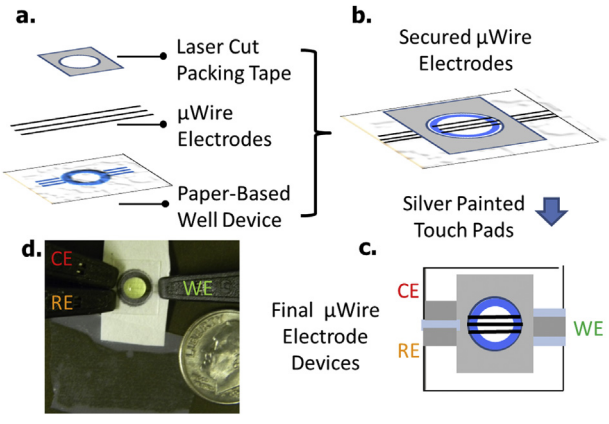
2. Experimental

2.1. Materials and equipment

Potassium chloride (KCl), potassium nitrate (KNO_3), potassium hydroxide (KOH), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), potassium ferricyanide ($K_3Fe(CN)_6$), 30% hydrogen peroxide (H_2O_2), acetone, sucrose and Whatman #1 filter paper were purchased from Fisher Scientific (Fairlawn, NJ). Potassium ferrocyanide ($K_4Fe(CN)_6$) was purchased from Mallinckrodt Chemical Works (St. Louis, MO). Graphite (<20-μm diamter) and D-(+)-glucose were purchased from Sigma (St. Louis, MO). Cellulose acetate and cyclohexanone were purchased from Sigma–Aldrich (St. Louis, MO). High-purity silver ink was purchased from SPI Supplies (West Chester, PA). D-(−) Fructose was purchased from Eastman (Rochester, NY). Glucose oxidase reagent set was purchased from Pointe Scientific (Canton, MI). Electrode materials, 99.99% pure gold (25 μm), platinum (30 μm), copper (25 μm), silver (25 μm), platinum with 8% tungsten (18 μm) and platinum with 20% iridium (15 μm) microwires (diameter), were purchased from California Fine Wire Company (Grover Beach, CA). All reagents were used as received without further purification. All electrochemical measurements were done using an eDAQ EA161 Potentiostat and EC201 e-Corder (Denistone East, Australia). Copier transparency sheets PP2200 and 2-in-wide Scotch® brand heavy duty clear shipping packaging tape were purchased from 3 M (St. Paul, MN). Devices were printed using a Xerox (Norwalk, CT) ColorCube 8870 wax printer and stencils, paper and tape components were cut using a 30 W Epilog (Golden, CO) Zing Laser Cutter and Engraver. All beverage samples were purchased from a local store and stored at 4 °C until use.

2.2. Microwire ePAD fabrication

ePADs were designed using CorelDRAW (Corel, Ottawa, Ontario), a graphic design program, and fabricated on Whatman #1 filter paper. Fluid flow and containment were achieved by printing hydrophobic wax barriers using a wax printer [9]. Wax printed designs of 4-pt line thickness were melted through the filter paper on a 150 °C hotplate for 90 s to create wax barriers. Packing tape was used to seal the bottom of the device and prevent leaking. On the printed side, microwires were spaced 1 mm apart across the device using the printed alignment marks as guides and taped in place (Scheme 1).



Scheme 1. Well-based ePAD fabrication showing (a) the device layers, (b) resulting side view of the device, (c) top view of the fabricated device with alternatingly covered and silver painted electrode ends, and (d) device image with electrode leads attached and 30 μL of solution in the 7 mm diameter well.