Interest in biofuel cells has increased in the past decade in pursuit of self energetically-sustained biomedical devices and also small, portable electrical devices capable of work by harvesting energy from natural fuel sources. Such interests exist due to the low temperature condensation reaction with H\textsubscript{2}O at room temperature. TMOS polymerization of the cathode surface was performed in a chemical vapor deposition process to form a silica-gel matrix. The gas diffusional cathode was assembled to a capillary driven microfluidic system to be electrochemically characterized. The characterization was performed from electrolyte pH 5 to pH 8 with increments of 0.5 in pH. The best performance was observed at pH 5.5 showing a current output of 655.07 ± 20.37 μA cm\textsuperscript{-2} and 205.37 ± 1.57 μA cm\textsuperscript{-2} at 0 V and 0.3 V, respectively. At a pH of 7.5 the current generated was 287.05 ± 146.18 μA cm\textsuperscript{-2} and 345.36 ± 30.04 μA cm\textsuperscript{-2} at 0 V and 0.3 V, respectively. The results show the stability of the enzymatic structure, subject to various pH, is maintained within the 3D-CNT silica-gel matrix for pH lower than 8. Future work will focus on storage life and stability over time.

The biocathode design is constructed by utilizing a dual layered electrode assembly that integrates composite nanomaterial constituting unique nano-architectures. This design was envisioned as a consequence of consideration for electrode materials to minimize ohmic and oxygen mass transfer losses. Toray paper (TP) modified with carbon nanotubes (CNTs) introduced by previous studies\textsuperscript{-23-26} were utilized as air-breathing biocathode materials. This type of material was used as the electrode due to their high conductivity, porous nanostructures, and surface area properties. The GDL has hydrophobic and porous properties to allow oxygen transport (XC35, 35\% tetfonized carbon powder) while the CL is thin and has a high surface area for enzyme loading and stability. A chemical vapor deposition (CVD) process was used to grow CNTs onto TP utilizing electrodeposited metal seeds which catalyze the reduction of the carbon source, ethylene, at a high temperature. The integration of the hydrophobic (XC35) and hydrophilic (TP-CNTs) layers allows efficient transport of oxygen. In order to maximize the proton mass transfer in the electrolytic solution and increase the cathode’s performance, the biocathode is assembled to a capillary-driven quasi-2D micofluidic system. This system facilitates the electrolytic solution transport to the cathode\textsuperscript{-27} by pumping the electrolyte solution by action of a liquid–vapor equilibrium with no external energy applied. Thus addressing ohmic resistance in electrolyte solution by supplying “fresh” electrolyte to the CL.

Bilirubin oxidase (BOx) enzyme is a multicopper oxidase that was selected because it is proven to work by a 4-electron DET.\textsuperscript{-29} The selection of DET mechanism is a result of the consideration to minimize kinetic losses of the catalytic system. Immobilization of BOx in silica gel matrix using tetramethyl orthosilicate (TMOS) resulted in the formation of a 3D nanomaterial that is efficient for electron transport.\textsuperscript{-30,31} The TMOS entrapment was believed to prolong the enzymes stability for approximately one month.\textsuperscript{-9} The silica gel surrounding the TP-CNTs surface formed a 3D CNTs network-gel matrix which is highly conductive, porous, and stable allowing the Bilirubin oxidase enzyme...
Experimental

**Apparatus.—** All experiments were conducted using a three-electrode cell by the common potentiostats: Gamry Reference 600 and 300 Potentiostat, Galvanostat/ZRA and Princeton Applied Research VersaSTAT 3 potentiostat/galvanostat. All potentials were reported versus Ag/AgCl (CH Instruments Inc. Cat. CH111) reference electrode, and Platinum mesh counter (Pt. 0.127 mm and purity 99.9% versus Ag/AgCl (CH Instruments Inc. Cat. CHI111) reference electrode). Characterization of materials was done using Scanning Electronic Microscope Hitachi (S-5200) equipped with Alfa-Aesar Cat. 10282). Characterization of materials was done using Scanning Electronic Microscope Hitachi (S-5200) equipped with Electron Diffraction Spectrometer (EDS). The tube furnace used was a Blue M model TF55030A from SPX-Thermal Product Solutions for the CVD of carbon nanotubes onto TP (within a quartz crystal tube). Plasma Cleaner/Sterilizer by Harrick model PDC-32G was used to operate between pH 5.5 (low acidic pH) and pH 7.5 (physiological pH).

**Materials.—** The manufacturer, Fuel Cell Earth LLC (Stoneham, MA.), of TGP-H-060 (Toray Paper) reported the material has a re-sistivity of 80 mΩ through the plane and 5.8 mΩ in the plane. The porosity was reported to be 78% with a thickness of 0.19 mm, and carbon fiber diameter of 5–10 μm. Bilirubin Oxidase (BOx) with enzyme unit 2.7 unit/mg was obtained from Amano Enzyme USA Co., Ltd. (Elgin, IL). Paper based setup consisted of Filter Paper from VWR International (North American Cat. No.:28310–128) with 15 cm diameter. The circuitry of the cell was painted on the filter paper with PELCO Colloidal Graphite water-based, isopropanol-based, and Fast Drying Silver Paint (silver in iso-butyl methyl ketone) from TED PELLA, INC. (Redding, CA). Scotch (3M St. Paul, MN) packaging tape (clear) was used as laminate to hold electrode in place along with generic painted paper clips.

Ethylene, Hydrogen and Nitrogen gas supplied from Argyle Welding Supply Inc. (Albuquerque, NM). Solutions of buffer, Nickel, Cobalt made with Nickel (II) acetate tetrahydrate (Ni(CH₃COO)₂), 99.998% metals basis, Cobalt (II) acetate tetrahydrate, reagent grade and Tetramethyl Orthosilicate (TMOS) were obtained from Sigma-Aldrich Co. (St. Louis, MO). Potassium phosphate (KP), monobasic and dibasic from EMD Chemicals Inc., with no further purification, were used to make KP buffer solutions (K-PB) of pH 5.5, 5.6, 5.7, 7, 7.5, and 8. Deionized water from Honeywell Burdick & Jackson (Muskegon, MI) was used to make all the electrolytic solutions.

**Metal catalyst deposition.—** Toray paper is a commercially available carbon fiber paper used regularly in biofuel cells. In order to deposit metal seeds on TP, we used an oxygen plasma cleaning process to absorb oxygen radicals on the paper making it hydrophilic. The TP-sample was placed within a plasma cleaner which is vacuum pumped to ~70 mTorr and activated for 12 seconds. Once this is done, TP was placed in a ring like stack cell with open faces and immersed into a beaker containing the mixture Ni(CH₃COO)₂ and Co(CH₃COO)₂ (solution a) or only Ni(CH₃COO)₂ solution (Figure 1). The solution was prepared by weighing out 2.5 grams of Ni(CH₃COO)₂ and/or CoNi(CH₃COO)₂ and dissolving it in 100 mL of water. Addition of 3.5 mL of acetic acid (20 N Molar) brought the solutions pH to 4. With the TP in place as the working electrode and Ni-mesh as counter electrode connected to a potentiostat, pulse chronoamperometry was performed. In order to control seed diameter and size, a potential of −1.3 V was applied by chronoamperometry in 8 steps of 2 seconds each (Figure 2).

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\text{Ni(H}_2\text{O)}_6^{2+} + 2e^- = \text{Ni}^0 + 6\text{H}_2\text{O}
\]  \[1\]

**Carbon nanotube growth by chemical vapor deposition.—** Chemical vapor deposition (CVD) was performed on the TP-Ni and TP-CoNi in order to grow CNTs. A crystal quartz tube was utilized as the chamber for deposition. Six pieces of TP-Ni were inserted into the glass tube. The pieces were separated by RVC of 80 grade porosity to provide spacing between TP-samples and allow the flow of gases. One RVC-“sacrificial” piece was used at the front (inlet) of the tube to avoid burning of TP-sample due to the initial temperature rise. The tube was placed in a tube furnace where an inlet and outlet hose were connected. The inlet gases were controlled by a gas flow controller where initially 5 mL/min hydrogen and 95 mL/min nitrogen gases flow. Once the flows stabilized a program was set to run on the furnace. During the first step, temperature was raised 10 °C/min up to 500 °C, and was held at 500 °C for 30 minutes. Then the temperature began to rise at a rate of 10 °C/min. When the temperature reached 620 °C, hydrogen gas was shut off and ethylene gas was fed at a rate of 35 mL/min while the flow of nitrogen gas was maintained. The temperature continued to rise during the gas switch and reached 750 °C where it was held for one hour. After the 750 °C exposure, the ethylene flow was shut off and the tube was left to cool down; the contents were removed once at room temperature. The results from Ni-seed deposition and CNTs growth observed under SEM are shown as Figure 3.

**Dual-layer assembly and Box-enzyme entrapment.—** As stated previously the design of an air-breathing cathode must have a porous

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Figure 1. Stack cell assembly for Ni-seed electrodeposition, isometric and side views.
Figure 2. SEM images of metal-seeds deposited on carbon fibers of TP with lower and higher resolution on the left and right, respectively. A) Ni seed deposition at pH4. B) Ni and Co seed deposition at pH7.

hydrophobic layer that was provided by packing 35% teflonized carbon powder (XC35). The carbon powder was packed at 1000 psi for 5 minutes using a hydraulic table press. 75 mg of XC35 was placed over the Toray paper along with 50 μL of ethanol. The powder was weighed out and placed in a die with the circular area of 2.27 cm² which was the area of CNT growth. This layer provided hydrophobic-ity that promotes constant oxygen gas diffusion toward the catalytic layer. This process was performed to create the XC-TP-CNTs electrode (where XC stands for XC35).

Enzyme was entrapped on the CNT-modified TP through the polymeric matrix formation of silica gel. First, 5 mg of BOx enzyme was dissolved in 200 μL of 0.1M K-PB, pH7.5 and dropped on the CNT

Figure 3. (A) (B) SEM image of plain TP (C) SEM images of TP-CNT-BOx cathode, (D) and TP-CNT-BOx-TMOS cathode.
modified TP surface. Box was allowed to physically adsorb overnight at 4°C. The following day the biocathode with Box was placed in a CVD chamber (9 cm diameter, 1.7 cm height) approximately 96 mL in volume. Two small caps were placed in the chamber, one with 1 mL of water and the other 200 μL of TMOS, for 5 minutes while having the catalytic layer of the CNT-modified TP exposed to the TMOS vapor. Later the chamber was sealed with parafilm and TMOS vapor diffused toward the exposed surface of the electrode along with water vapor reacting to form a silica-gel matrix. Five minutes of deposition formed an adequate thickness to entrap the enzyme and allow gas and electrolytic solution diffusion to the enzyme. After the TMOS deposition the cathodes which contain the Box dissolved in K-PB were stored in a refrigerator overnight at 4°C, and TMOS was still reacting on the surface of the electrodes to form silica gel.

**Paper-based cathode microfluidic system ensemble.**—The air-breathing cathodes were assembled to a capillary driven quasi 2D microfluidic system. The system consists of a filter paper cut out that resembles a fan of 270°-semicircular shape (Figure 4). The biocathode and Pt-counter electrode were laminated on the fans leg using packaging tape cut in a rectangular shape with an inner-circular cut out that allows the exposure of the hydrophobic layer (Xc35) of the cathode to the air (Figure 4A). After the assembly of the cathode to the fan, the section of the fans leg that is not laminated was immersed in the K-PB solution contained in a manufactured 50 mL-cell (Figure 4B). K-PB was driven past the catalytic layer constituted by the Box enzyme entrapped within the CNTs network-3D silica matrix on the CNTs-modified TP. The flow of the electrolytic solution is driven by capillary action characteristic of the filter paper material and maintained by the pumping effect sustained by the liquid-vapor equilibrium of the semicircular-fan shape.

**Study on pH dependency by electrochemical characterization.**—The thermodynamic behavior of the enzymatic system of the biocathode was evaluated by open circuit potential measurements (OCP). The potential was monitored against time at zero applied current density. The measurements were performed for 1 hour on the biocathode previously stored overnight. The electrolytic solution consisted of 0.1M K-PB ranging from pH 5 to pH 8. The electrodes tested were TP-CNTs, TP-CNTs-Box, and TP-CNTs-Box-TMOS. The OCP was measured in the three-electrode setup using the half fan cell (Figure 4). Immediately following the OCP measurements, chronoamperometric (CA) measurements were performed from 0.55 V to 0 V in decreasing applied steps of 50 mV. Each potential was applied for 500 seconds which allowed the system to reach steady-state. The generated currents were used to plot polarization curves as potential vs. current to analyze the biocathodes performance (Figure 5).

**Results**

**Metal seed deposition.**—In order to increase the surface area of the TP, CNTs were grown on the surface of the carbon fibers of TP. This was achieved by depositing Ni and Ni-Co seeds onto the fibers which catalyzed the reduction of ethylene gas forming CNTs. A range of solutions with varying pH and metal compositions including Ni, Ni-Co, and Fe were attempted (not shown) to form metal seeds. The metal solutions of Ni pH4 (Figure 2A) and Ni-Co pH7 (Figure 2B) were used to produce metal nucleation’s. Ni seeds deposited at pH4 nucleated into seeds having a defined shape and regular size (35–60 nm diameter, Figure 2A). Ni-Co seeds deposited at pH7 nucleated into seeds having an agglomerated shape and larger size (70–120 nm diameter, Figure 2B). This result led to the use of Ni pH4 seeds exclusively for CNT growth for the cathode by considering the CNTs grown will have a uniform thin-diameter distribution.

**Carbon nanotube growth.**—Growth of CNTs on the TP occurred at 750°C by CVD with ethylene as the source of carbon. As expected the Ni-seeds deposited at pH 4 resulted in uniform distribution of CNTs throughout the TP-fibers. An abundant forest of CNTs can be seen in the SEM images of Figure 3C. A visible circular area of growth (Figure 3A) was also observed which corresponds to the circular area of Ni seed nucleation. The CNTs observed under SEM range from 65 nm to 100 nm in diameter. SEM provides visual evidence that the desired result of this growth was achieved and increased the surface area of the TP (compare to plain TP, Figure 3B), similarly to previous report of CNTs modified TP employed on anode design.21

**pH-dependence study.**—The Box-enzyme entrapped in the silica-gel matrix on the CNTs-modified TP electrode was subjected to pH-dependency study. The performance of the system was analyzed employing K-PB of pH 5, 5.5, 6, 6.5, 7, 7.5, and 8 as electrolytic solution. The K-PB solution serves as electrolyte and source of protons needed to reduce molecular oxygen to water at the multi-copper active site of the Box. When comparing the polarization curves obtained by chronopotentiometry, the performance of the biocathode employing the electrolytic solution at low pH shows the highest generated current density (i.e. pH 5.5, in Figure 5B). According to the manufacturer of Box, the isoelectric point (pl) of the enzyme is at pH 4.1, and pH 6 is the pH at which the enzyme shows the highest activity or optimal activity. Correlating those results, it is possible to determine that the Box 3D-structure has a net negative charge at pH 5.5 (pH 4.1).
Figure 5. A) pH-dependency study for TP-XC35-CNT-Box-blanks in phosphate buffer pH 7.5, B) polarization curves for the TP-XC35-CNT-Box-TMOS cathode in phosphate buffer pH range 5 to 8, and C) pH-dependency study performance points at 0.3 V for the TP-XC35-CNT-Box-TMOS cathode in phosphate buffer pH range 5 to 8.

Table I. Performance of XC-TP-CNTs-BOx-TMOS at different pH at 0.3 V and 0 V.

| pH  | Current (μA.cm$^{-2}$) at 0.3 V | Current (μA.cm$^{-2}$) at 0 V |
|-----|------------------------------|-------------------------------|
| 5   | 312.77 ± 51.47               | 495.89 ± 34.63               |
| 5.5 | 345.36 ± 30.04               | 655.07 ± 146.18              |
| 6   | 266.77 ± 20.37               | 439.32 ± 29.54               |
| 6.5 | 282.33 ± 69.37               | 466.81 ± 36.01               |
| 7   | 248.72 ± 46.11               | 376.06 ± 49.24               |
| 7.5 | 205.37 ± 1.57                | 287.048 ± 20.37              |
| 8   | 155.1 ± 15.47                | 148.05 ± 36.7                |

> pI) which, at the same time, is a pH < optimal pH reported by the manufacturer. These results show the 3D structure of the enzyme obtained by induction of the electronic distribution of the nanoarchitecture of the CNTs-network 3D-silica gel matrix is highly active, enhancing electron transfer and H$^+$ diffusion at pH 5.5 compared to the other pHs analyzed herein. The pH of highest performance observed in this study (655 ± 146.18 μA.cm$^{-2}$ at 0 V and 345.36 ± 30.04 μA.cm$^{-2}$ at 0.3 V for pH 5.5, Figure 5B and Table I) is found to be between the pI and the optimal pH reported by the manufacturer (pI 4.1 < pH 5.5 < pH 6). Additionally, studies have reported that at pH < 7.5 the kinetics of condensation of the silica gel is higher than at basic pH (≥8); furthermore, the dissolution of silica gel is kinetically higher at pH > 7.5. Then, having the electrolytic solution at pH > 7.5 would confer stability to the silica matrix on the electrode surface, enhancing the enzyme stability in the pH range. At pH 8 the electrode shows the lowest performance (Figure 5C) which is correlated to dissolution of the silica gel, releasing the enzyme from the surface. The stability of the silica gel as a function of the pH is observed in the behavior/ enzymatic performance of BOx in Figure 5C where the cathodes show a higher current generation between pH 5 and 7.5 and high decrease of activity at pH 8.

When comparing to other cathode designs, this design shows improved performance versus gas-diffusional cathodes not employing CNTs. At pH 7 the current generated of 248 μA.cm$^{-2}$ is increased with respect to previous gas-diffusional designs employing XC35-Box and carbon ink-Box assembled to paper-based microfluidic systems that generated approximately 197 μA.cm$^{-2}$ and 118 μA.cm$^{-2}$, respectively (at 0.3 V and pH 7). Furthermore, the design shows a current density of 345.56 μA.cm$^{-2}$ at pH 5.5 which is comparable to the performance of cathodes introducing high conductive bucky paper (commercial CNTs-based paper) which show a current output of approximately 345.56 μA.cm$^{-2}$ at pH 7.

The analysis of the performance of the biocathode at physiological pH of 7.5 is of relevance while considering the device to be employed in biomedical applications. The polarization curve at pH 7.5 (Figure 5B) presents 287.05 ± 20.37 μA.cm$^{-2}$ at 0 V and 205.37 ± 1.57 μA.cm$^{-2}$ at 0.3 V and the smallest fluctuations while considering reproducibility of the design, deduced by the low statistical deviation and residual values (Table I).

Conclusion

This research has shown that the process of growing CNTs on electrode material, Toray paper, is reproducible and the nanostructured architecture of the catalytic layer can be tailored or engineered to provide a favorable environment for the active enzymatic structure and confer stability within range of pH 5 to 7.5. The CNT growth increases the available surface area for increased enzyme loading and stable entrapment. SEM observations provide topographic evidence of CNT growth, enzyme adsorption and entrapment. Chronoamperometric experiments done on blank cathodes (i.e. no BOx enzyme) and fully developed biocathode’s designs confirm that there is reproducible enzymatic activity with full designs. As the pH of the K-PB buffer was increased from 5 to 8 performance varied due to conformational changes induced by the environment surrounding the
enzymatic structure, and the silica gel matrix degrades at pH higher than 7.5 showing decrease of current generation (i.e. pH 8). Maximum current output was observed at pH 5.5 while the most consistent and reproducible current density was obtained at a pH of 7.5. At pH 7.5, the cathode performed satisfactorily at the expected operating potential of 0.3 V giving a current density of 205.37 ± 1.47 μA.cm⁻². This biocathode design is suitable for use in biofuel cells for biomedical application testing. Future studies of the stability of this design are expected to confirm preliminary results of the enzyme stability within the CNTs-network 3D-silical gel matrix and will be re-evaluated over a period of 6 months.

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