ELECTRONIC SUPPLEMENTARY INFORMATION

Soft, stretchable, high power density electronic skin-based biofuel cells for scavenging energy from human sweat

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Experimental Section

Reagents and instrumentations

Silver oxide (Ag_2O) powder, 1,4-naphthoquinone (NQ), bovine serum albumin (BSA), glutaraldehyde, L (+)- Lactic acid, potassium phosphate dibasic (K_2HPO_4), potassium phosphate monobasic (KH_2PO_4), ethanol, and acetone were purchased from Sigma-Aldrich. (St. Louis, MO). L-Lactate oxidase (LOx) (activity, 106 U/mg) was procured from Toyobo Corp. (Osaka, Japan) while multi-walled carbon nanotubes (MWCNTs) (purity > 95%, diameter = 10-20 nm, length = 10-30 µm) was obtained from Cheap Tubes Inc., Grafton, USA. Ecoflex® 00-30 (Smooth-On, Inc., PA) was prepared in-house by mixing equal volumes of pre-polymer A with prepolymer B provided by the supplier. Carbon ink (E3449) were obtained from Ercon Inc (Wareham, MA, USA). Ultra-pure deionized water was used to prepare all the reagents and electrolytes. Electrochemical experiments were performed using a μAutolab Type II controlled by NOVA software version 1.11. Optical images and videos were captured using a digital camera (Nikon, D7000).

Fabrication of E-BFC electrodes

A 4" Silicon wafer was spin coated with polymethyl methacrylate (PMMA A2) from MicroChem at 3000 rpm for 30 s and then soft baked at 180 °C for 1 min. Poly(pyromellitic dianhydride-co-4,40 -oxydianiline) amic acid solution, PI 2545 precursor (PI) from HD MicroSystems was then spun coated at 4000 rpm for 45 s, soft baked on a hotplate at 110C for 1 min and 150 °C for 5 min. Subsequently, the film was cured in a vacuum oven at 240 °C for 1.5 hours.

Metallization of 10 nm/550 nm/20 nm/100 nm – Ti/Cu/Ti/Au was done with a sputter coater (Denton 18/Denton 635). Metal layers were then defined using photolithography (photoresist (PR) AZ 1512, spun at 3000 rpm for 30s, soft baked at 100 °C for 1 min). Exposure was done via an i-line mask aligner (SussMicrotec MA6) for 60 mJ dose. The exposed film was then developed by immersion method in TMAH tetra methyl ammonium hydroxide developer (AZ 300 MIF). The developed pattern was then etched using potassium iodide gold etchant for gold (Transene Gold Etch TFA), buffered oxide etchant (6:1) for titanium, and 0.5 mol/L ferric chloride solution for copper. PR was then removed using acetone and isopropyl alcohol.

An additional layer of PI was spin coated. Once fully cured, the PI was defined by photolithography (PR AZ 1529 spun at 2000 rpm, cured at 110 °C for 3 min, developed in AZ MIF 300 developer using immersion method). Dry etching was done (100 mTorr, O_2 50 sccm, 100

W for 5 min) in such a way that the serpentine bridges were fully covered by the PI while the circular islands were exposed. The two layers of PI encapsulate both top and bottom surfaces and sidewalls of the serpentine electrodes. Silicone substrates (Ecoflex, 250 μm thick) were prepared by mixing the two components in a 1:1 weight ratio. Silicone mixture was spin casted at 300 rpm for 60 seconds on a glass slide coated with poly(methy lmethacrylate) (PMMA495 A2 at 3000 rpm for 30 s, 180 °C for 2 min) and then cured at room temperature for 2 h.

The serpentine electrodes were then released by dissolving PMMA sacrificial layer in hot acetone (90 °C). The released devices were then picked up from the Si wafer using water soluble tape. Thereafter the devices were mounted on a glass slide with exposed sides facing up. Titanium (3 nm) and silicon dioxide (30 nm) were sputtered onto circular islands using a Kapton film shadow mask. Both top surface of silicone substrate and bottom surface of copper electrodes were activated in UV ozone for 2 min, and the copper electrodes were laminated onto the substrate. The cellulose water soluble tape was removed by rinsing with DI water until it fully dissolved.

Electrodes preparation of anode and cathode

Anodes were obtained by mixing of 8mg MWCNTs and NQ mixture (35mg : 10mg ratio) with 10μL glutaraldehyde (1%) and 50μL of a Chitosan (3 wt% in 1M acetic acid) solution in acetic acid (0.1M) to obtain a homogeneous composite material. The homogenous paste was then molded into circular anodic pellets (height = 1mm; diameter = 2mm) using a stencil designed in AutoCAD (Autodesk, San Rafael, CA) and outsourced for fabrication on stainless steel through-hole 12 in. x 12 in. framed stencils (Metal Etch Services, San Marcos, CA). Cathodic pellets were fabricated in a similar fashion by using a paste comprising of a mixture of 8mg MWCNTs and Ag_2O mixture (70mg: 30 mg ratio) with 80µL of a Nafion solution in an ethanol (2%).

Thereafter, carbon ink was screen printed on the stretchable E-BFC by using an MPM-SPM semiautomatic screen printer (Speedline Technologies, Franklin, MA). The carbon ink was cured at 80 °C for 10 min in a convection oven. Subsequently, anodic and cathodic pellets were bonded to the carbon layer via conductive carbon glue (TED PELLA, Inc. Prod. No: 16050). The anodic pellets were then functionalized with enzyme by drop casting 5µL of the LOx solution (40 mg ml^{-1} containing 10 mg ml^{-1} BSA) on each electrode and allowing the solution to dry under ambient conditions. Finally, each electrode was covered with 2 µL of 1 wt% chitosan solution prepared in 0.1M acetic acid.

Fabrication of customized Bluetooth device.

To demonstrate that the proposed BFC can power a practical wearable device, a custom circuit board featuring a Texas Instruments CC2451 Bluetooth Low Energy (BLE) radio and microcontroller System-on-Chip (SoC) was developed. Since the voltage of the BFC was lower than what was required to power the BLE SoC, the circuit board also featured a Texas Instruments BQ25504 boost converter to step-up the BFC voltage to a higher value. Due to the high peak-to-average power draw of the BLE SoC (in operation, peak power exceeded 10 mW), the output of the boost converter was decoupled by a 2.2 mF energy-buffering capacitor, selected as a trade-off between size, buffering capacity, and standby current leakage. During system start-up, the BLE radio was disconnected until the capacitor voltage exceeded 3.5 V. When first connected, the radio underwent an initialization routine, and was then programmed to transmit a beacon once per second at an average power consumption of 0.4 mW. Transmitted data was received and demodulated by a computer equipped with a Texas Instruments BLE to serial dongle, and displayed via a custom MATLAB script.

Mechanical and stretching test

The mechanical resiliency studies were conducted on a motorized linear stage connected to a controller (A-LST0250A-E01 Stepper Motor and Controller, Zaber Technologies, Vancouver, Canada). The E-BFCs were repeatedly stretched by 50% at a speed of 0.1 $cm \cdot s^{-1}$ from 0% to 50% and back to 0% as one cycle. The speed and length of the physical strain were programmed via scripting software (Zaber console, Zaber Technologies, Vancouver, Canada). The current and voltage was recorded by interfacing the E-BFC to a Keithley 6514 system electrometer while the E-BFC was repeatedly stretched. Studies pertaining to powering of LED by the E-BFC under repeated stretching relied on employing a custom-built DC/DC converter PCB to boost the output voltage to 3.2V. Details about the DC/DC converter is discussed in our previous work.[45] E-BFCs were subjected to mildly stirred 14mM lactate solution for all the mechanical resiliency studies.

On-body power generation.

E-BFCs were coated with PVA gel prepared as follows. A 5.0% w/v PVA solution was prepared in deionized water by heating the solution to 120 °C to dissolve the polymer followed by cooling down the suspension to room temperature. After the mixture was cooled down, it was placed in an ice bath and the pH was adjusted to pH 1.0 by adding 5 M hydrochloric acid. Subsequently, glutaraldehyde was added to give a final concentration 0.5% w/v. The final mixture was then stirred for 1 min and poured onto the glass mold. The gel was allowed to form at −20 °C freezer overnight. The on-body performance of the epidermal skin-based biofuel cells was evaluated in strict compliance with the protocol approved by Institutional Review Board (IRB) at the University of California, San Diego. The study was performed by healthy volunteers having no prior medical history of heart diseases, diabetes, or chronic skeletomuscular pain; a signed consent was obtained from each volunteer following thorough prescreening procedure. Volunteers were asked to wear the E-BFC on their deltoid or upper trapezius muscle to assess real-time power generation. Subjects were then asked to begin cycling on a stationary cycle at a steady, comfortable rhythm. The resistance of the cycling activity was increased at 3 min intervals and the absolute resistance intensity profile was selected based on subject's fitness level. Following the bout, the subjects were instructed to gradually slow down their cadence during a 3 min "cool-down" period whereby the resistance was reduced to low level. The real-time power generated by the E-BFC was recorded by connecting a load (1 kΩ) across the E-BFCs. The value of the resistor that could extract the highest power was identified based on the power curves obtained for the E-BFCs (Fig. 2F). Electrical current passing through the resistor was recorded every 1 s using a multimeter (Agilent 6 ½ digit model 34411A and Keysight BenchVue software (version 3.0). The study involving powering of a LED relied on attaching the skin-worn E-BFC to the a DC/DC converter that boosted the output voltage to power the LED.

Sr. No.	**System**	**Maximum Power Density ($\mu W/cm^2$) with lactic acid as fuel**	**Reference**

1	Anode: Lactate oxidase/Tetrothiafulvalene/CNT Cathode: Platinum Black	~50 (20 mM fuel)	1
2	Anode: Lactate oxidase/Tetrothiafulvalene-7,7,8,8-tetracyanoquinodimethane/CNT Cathode: Platinum Black	~100 (20 mM fuel)	2
3	Anode: Lactate oxidase/carbon cloth Cathode: Platinum coated carbon cloth	~400 (50 mM fuel)	3
4	Anode: Carbon fiber/Graphene/Meldola's Blue/SiO_2 NPs/Lactate Dehydrogenase Cathode: Carbon fiber/Graphene/Hemin/SiO_2 NPs/Lactate Oxidase	~380 (14 mM fuel)	4
5	Anode: Au microwire/AuNPs/Cellobiose Dehydrogenase Cathode: Au microwire/AuNPs/Bilirubin Oxidase	~0.26 (sweat + 500 µM glucose)[a] [a]Glucose in sweat is used as fuel	5
6	Anode: 3D Carbon nanotube-Naphthoquinone pellet/Lactate oxidase Cathode: 3D Carbon nanotube-	~1200 (20 mM fuel)	Present work

	Silver oxide pellet		

Table 1: Comparison of previously reported wearable biofuel cells with the present work.

Supplementary Figures

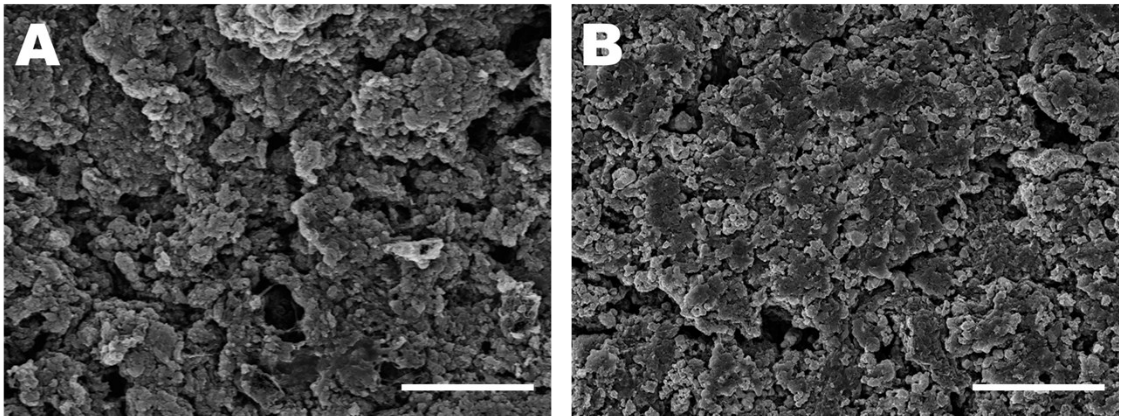

Fig. S1: SEM images of (A) anodic and (B) cathodic pellets. Scale bar = 50 µm.

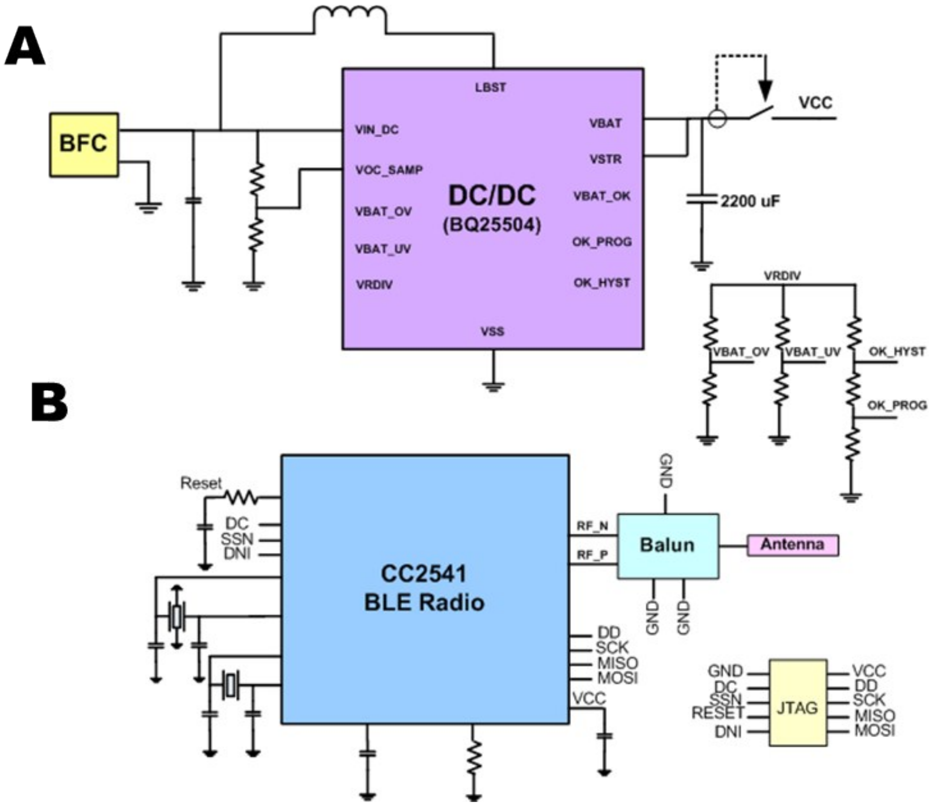

Fig. S2: Circuit diagrams for the (A) DC-DC converter and the (B) BLE device.

Supplementary videos

Video S1: Powering of a LED by an E-BFC subjected to repeated stretching (ε = 50%).

Video S2: Effect of repeated stretching (ε = 50%) of an E-BFC to it's short-circuit current.

Video S3: Effect of repeated stretching (ε = 50%) of an E-BFC to it's open circuit voltage.

Video S4: Powering of a LED by an E-BFC harnessing energy from a human subject's sweat.

References

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