Supporting Information for

Hybrid Glucose/O_2 Biobattery and Supercapacitor Utilizing a Pseudocapacitive Dimethylferrocene Redox Polymer at the Bioanode

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Experimental Methods

The bioanodes were adapted from published procedures (1-2). A volume ratio of 1 $FcMe_2$–LPEI (10 mg mL^{-1}): 0.44 FAD-GDH (30 mg mL^{-1}, E.C. 1.1.99.10, Aspergillus sp., Sekisui

Diagnostics): 0.54 EGDGE (10% v/v) were mixed with 4 mg MWCNTs (Cheaptubes) per cm^2 geometric electrode area. Total volume was 200 µL per cm^2. The solution was brushed onto carbon felt (Alfa Aesar) electrodes and left to dry overnight at room temperature.

The biocathodes were adapted from previously reported protocol (3). 1.5 mg BOx (E.C. 1.3.3.5, *Myrothecium sp*., Amano Enzyme) were suspended in 75 µL of 200 mM citrate/phosphate buffer, pH 6.5, then added to 7.5 mg of anthracene modified MWCNTs. The mixture was repeatedly vortexed (1 min) and sonicated (15 s), four times. Finally, 25 µL of TBAB-modified Nafion® was added to the mixture and vortexed and sonicated one more time. The final mixture was brushed onto three carbon felt electrodes(approximately 33 µL per 0.25 cm^2 electrode)and left to dry for 2 hours.

The anode and cathode were tested individually in a three-electrode setup with a saturated calomel reference electrode (SCE) and platinum mesh counter electrode. To equilibrate the $FcMe_2$-LPEI on the anode, ten 50 mV s^{-1} CVs followed by five 10 mV s^{-1} CVs were taken from -0.25 to 0.75 V vs SCE in 200 mM phosphate/citrate buffer, pH 6.5. Then, 1 M glucose (rotated overnight) in 200 mM phosphate/citrate buffer, pH 6.5 was injected into the cell for total concentrations of 0, 100, and 200 mM glucose to confirm bioelectrocatalysis. The cathode was tested for bioelectrocatalysis with 5 mV s^{-1} CVs taken from 0.7 to 0.1 V vs SCE in N_2 sparged, air-equilibrated, and O_2 sparged 200 mM glucose and buffer. Anode capacitance was measured using constant current charge/discharge in 200 mM phosphate/citrate buffer, pH 6.5.

Electrodes were soaked in fuel solution (O_2 sparged 200 mM glucose and buffer), then placed in a CR2032 Li-air battery stainless steel case (MTI), with Whatman filter paper #1 between them as a physical separator. The cathode side of the casing was mesh to allow air to enter the

cell. The casing was sealed with a crimping press, and additional fuel solution was injected through the mesh with a syringe.

The device's battery performance was analyzed by first measuring the open circuit potential (OCP), then performing 1 mV s^{-1} linear polarization from the OCP to 0.01 V to obtain polarization and power curves. The device's capacitance was evaluated by constant current charge/discharge at various discharge rates, current pulse chronopotentiometry with various current pulses and recovery times, and cyclic voltammetry at various scan rates from the OCP to 0.01 V.

Cyclic Voltammetry of Control Anodes

Controls of unmodified Toray paper as well as Toray paper modified only with the cross-linked polymer (*i.e.* no enzymes present) were investigated. Electrodes based on unmodified Toray paper do not exhibit a significant redox signal, and the addition of glucose to $FcMe_2$-LPEI-only anodes does not result in a significant bioelectrocatalytic current.

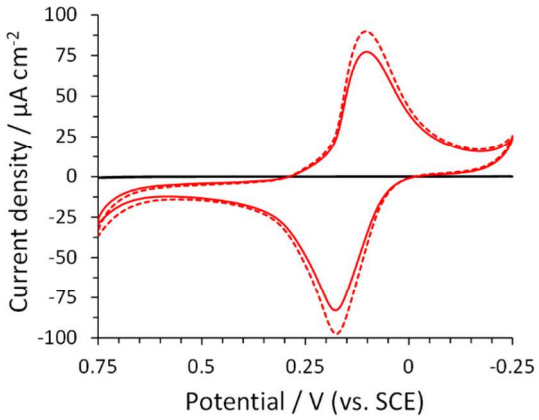

Figure S1. Overlay of 10 mV s^{-1} CVs for an unmodified Toray paper electrode (solid black line) and Toray paper electrodes with cross-linked 0.7 mg cm^{-2} $FcMe_2$-LPEI (no enzyme present) in buffer (solid red line), and in a solution of 200 mM glucose in buffer (dashed red line).

Cyclic Voltammetry of Bioanodes with Various Polymer Loadings

CVs corresponding with the CCDs in Figure 1a in the main text are shown in Figure S2, in which current density increases with increased polymer loading.

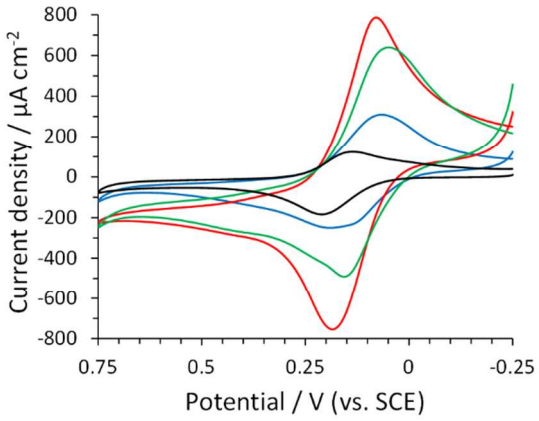

Figure S2. Overlay of 10 mV s^{-1} CVs for FAD-GDH anodes on Toray paper with various loadings of $FcMe_2$-LPEI in 200 mM phosphate/citrate buffer, pH 6.5. Loadings are 0.7 mg cm^{-2} (black line), 1 mg cm^{-2} (blue line), 3 mg cm^{-2} (green line), and 6 mg cm^{-2} (red line).

Optimization of MWCNT Loading in Bioanode

The loading of MWCNTs in the bioanode was optimized by testing anodes with a range of 0 to 16 mg MWCNT cm^{-2} geometric electrode surface area. As shown in Figure S3, the optimal loading was found to be 4 mg cm^{-2}, which further increased bioanode specific capacitance to 105 ± 10 F g^{-1}.

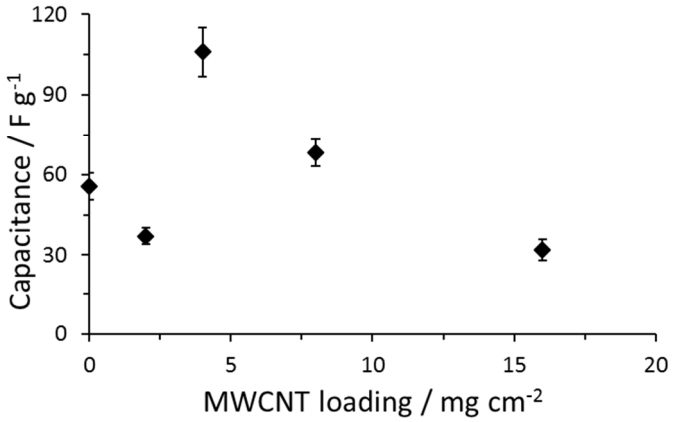

Figure S3. Capacitance calculated from constant current charge/discharge curves and normalized by mass of active material plotted *versus* the loading of multiwalled carbon nanotubes (MWCNTs) for FAD-GDH anodes cast on carbon felt with 6 mg/cm^2 $FcMe_2$-LPEI loading.

Cyclic Voltammetry of Carbon Felt Bioanode without MWCNT

In bioanode CVs where MWCNTs are present, there appear to be two overlapping reductive ferrocene peaks. This appears to be an effect of the MWCNTs creating a second redox environment for the ferrocene pendant. An adsorption effect occurs where the reduced ferrocene moiety is not particularly water-soluble and thus is partially adsorbed onto the MWCNT surface. Figure S4 shows CVs of bioanodes made without any MWCNTs, in which only a single reductive ferrocene peak is observed.

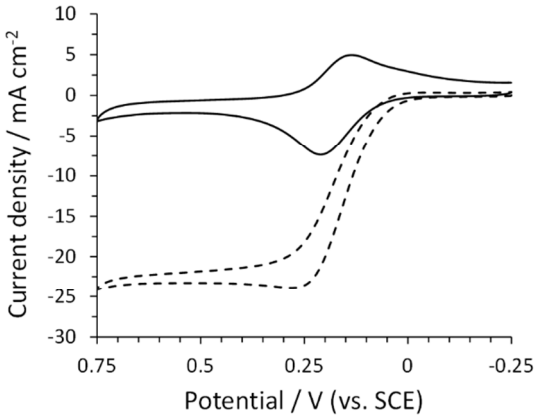

Figure S4. Overlay of 10 mV s^{-1} CVs for FAD-GDH / $FcMe_2$-LPEI carbon felt anodes without MWCNT in buffer (solid line), and in a solution of 200 mM glucose in buffer (dashed line).

REFERENCES

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2. Milton, R. D.; Lim, K.; Hickey, D. P.; Minteer, S. D. Employing FAD-Dependent Glucose Dehydrogenase Within a Glucose/Oxygen Enzymatic Fuel Cell Operating in Human Serum. *Bioelectrochemistry* **2015,** *106*, 56-63.

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