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ARTICLE TYPE

# Supplementary information

## Experimental Section

*Materials*

Synthesis of the redox polymers was achieved by adapting literature procedures[1] using $(NH_4)_2OsCl_6$ (Aldrich) as starting material to prepare the *cis*-Os(4,4'-dimethoxy-2,2'-bipyridine)$_2Cl_2$ and *cis*-Os(4,4'-dichloro-2,2'-bipyridine)$_2Cl_2$ complexes, which were then complexed, via ligand substitution reaction in ethanol/water solvent, to a previously pre-synthesised polyvinylimidazole (PVI) polymer.[2] Glucose oxidase (GOx) from (*A. Niger*) was obtained from Sigma – Aldrich and *Th*Lacc was donated by VTT Technology, Finland (K. Kruus). Unless otherwise stated all other chemicals were obtained from Sigma-Aldrich. All buffers were prepared from solutions of the selected base then adjusted to the desired pH using solutions of the acid.

*Apparatus*

Graphite disc electrodes (3 mm diameter), formed by shrouding graphite rods (Goodfellow) in glass tubes using heat-shrinkable tubing and establishing an electrical connection to copper rods (Farnell) at the rear with silver epoxy resin (Farnell), were used as working electrodes. Cyclic voltammetry was carried out with a CHI 650 potentiostat, using a graphite electrode, Ag/AgCl (3 M KCl) and platinum wire as working, reference and counter electrodes, respectively (IJ Cambria). EFCs were assembled by insertion of anode and cathode into a compartment-less electrochemical cell containing 5 mL of electrolyte solution. The anode and cathode were externally connected through a resistance box (IET Labs) over a resistance range of 5 MΩ to1 kΩ, and the voltage between the electrodes measured with a multimeter (Keithley) for each load.

Film assembly was monitored at each step with a quartz crystal microbalance (QCM, USI Japan) with 9 MHz QCM resonators (AT-cut, International Crystal Mfg). The gold resonators were first treated with 4 mM 3-mercaptopropionic acid in ethanol overnight to form negative monolayer surface to mimic graphite surface. Films were assembled onto negatively charged gold resonator surface and were dried in a stream of nitrogen before measuring the frequency change (ΔF).[3]

*Enzyme activity*

Glucose oxidase was obtained from Sigma – Aldrich (10 mg/ml stock solution was prepared in phosphate buffer pH 7.4) and *Trametes hirsuta* (*Th*Lacc) was provided by VTT (Finland) as (3.6 mg/mL) stock solution in citrate buffer pH 5. Enzyme activity was calculated using spectrophotometric assays (Agilent 8453). Glucose oxidase activity was monitored at 460 nm, where the increase in absorbance is a result of the oxidation of dianisidine through a peroxidase coupled system, using an extinction coefficient of 11300 $M^{-1}$ $cm^{-1}$, in phosphate buffer pH 6.[4] The enzymatic activity of the laccase was measured by monitoring the oxidation of 5 mM ABTS in 50 mM acetate buffer pH 4.5 at 420 nm over a period of 10 minutes using extinction coefficient of 36 000 $M^{-1}$ $cm^{-1}$.[5]

*Methods*

Electrodes were prepared, based on LBL self assembly of redox polymer and enzyme.[6] For anode and cathode 10 µL redox polymers (8–10 mg/ml solution/suspension in water) were adsorbed over graphite electrode for 20 minutes, then rinsed with milli Q water. Further enzymes 10 µL GOx of 10 mg/ml (1500 U/ml), or *Th*Lacc (390 U/ml) was adsorbed for 20 minutes, then washed with Milli Q water, further repeating these steps to form (polymer /enzyme)$_n$ films. Prepared films were dried for 12 h before testing electrochemically or EFC assembly. Unless otherwise stated, current and power densities were measured at 37 °C in 0.1M potassium phosphate buffered solutions containing 0.15 M NaCl, 0.1 M glucose and saturated $O_2$.

## Supplementary figures

**Figure S1.** QCM frequency shifts for alternate redox polymer – enzyme a) polymer I/GOx and b) polymer II/*Th*Lacc adsorbed on gold resonators first coated with a monolayer of 3-mercaptopropionic acid rendering a negatively charged surface that mimics the self assembly at graphite electrode.

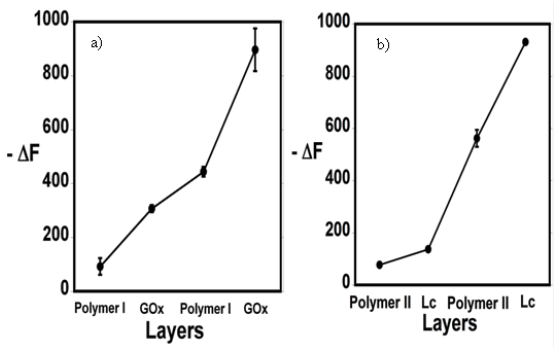
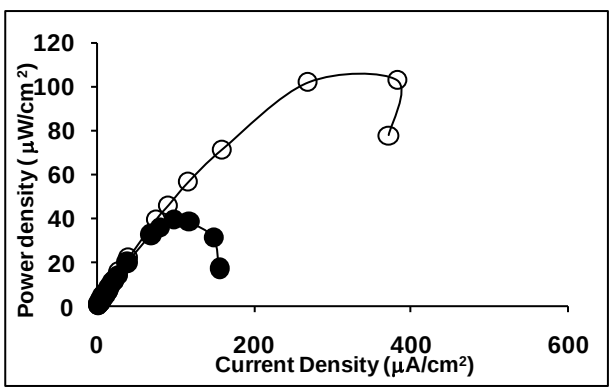



**Figure S2.** Power versus current density curve of an EFC composed (polymer I /GOx)$_2$ and (polymer II/ *Th*Lacc)$_2$ films in oxygen-saturated 0.1 M potassium phosphate buffer containing 0.15 M NaCl at 37 ºC, in the presence of 0.1 M glucose at pH 7.4 (closed circles) and 5.5 (open circles).



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