Electronic Supplementary Information (ESI):

Use of Low Cost and Easily Regenerated Prussian Blue Cathodes for Efficient Electrical Energy Recovery in a Microbial Battery

Xing Xie\textsuperscript{a}, Meng Ye\textsuperscript{a}, Chong Liu\textsuperscript{b}, Po-Chun Hsu\textsuperscript{b}, Craig S. Criddle\textsuperscript{ac} and Yi Cui\textsuperscript{bd}

\textsuperscript{a}Department of Civil and Environmental Engineering, Stanford University, 473 Via Ortega, Stanford, CA 94305, USA. E-mail: ccriddle@stanford.edu; Tel: +1-650-723-9032

\textsuperscript{b}Department of Materials Science and Engineering, Stanford University, 476 Lomita Mall, Stanford, CA 94305, USA. E-mail: yicui@stanford.edu; Fax: +1-650-725-4034; Tel: +1-650-723-4613

\textsuperscript{c}Woods Institute for the Environment at Stanford, Stanford University, Stanford, California 94305, USA.

\textsuperscript{d}Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Rd, Menlo Park, CA 94025, USA.

\textsuperscript{‡} These authors contributed equally to this work.
Materials and Methods

**PB electrode preparation.** Iron ferricyanide (Fe[Fe(CN)₆]) nanoparticles were synthesized by a simple and scalable solution-based chemical reaction. Specifically, 0.5 M potassium ferricyanide (K₃[Fe(CN)₆]) and 0.5 M ferric chloride (FeCl₃) were mixed in hydrochloride acid solution with pH 2. After 24 hours, the green precipitate was collected by centrifugation, washed three times with deionized water, and dried in a vacuum oven. A slurry was created by mixing dried green powder (85% wt), conductive carbon black (Super-P, TIMCAL, 8% wt) and PVDF (Sigma-Aldrich, 7% wt) in NMP (Sigma-Aldrich) were mixed and stirring overnight. The slurry was coated onto a piece of carbon cloth current collector (3 cm × 3 cm, Fuel Cell Earth, LLC). The coated carbon cloth electrodes were dried in a vacuum for 2 days, resulting in a total mass loading of ∼60 mg. The electrodes were then reduced electrochemically in a phosphate buffer solution (PBS, pH 7) to 0 V vs. Ag/AgCl with 0.5 mA current. The resulting PB electrodes were exposed to air overnight before use.

**MB construction and operation.** Two single-chambered, membrane-free MB reactors were fabricated: one was a plate-shaped plexiglass chamber of 3 cm × 3 cm × 0.3 cm \(^{S1}\); the other was simply a 100-mL glass bottle. The anode was a carbon cloth (3 cm × 3 cm, Fuel Cell Earth) microbial anode that was pre-cultured and producing current in a classic H-shaped MFC for more than 3 months \(^{S2}\). The original inoculum was domestic wastewater from the Palo Alto Regional Water Quality Control Plant. The cathode was the PB electrode. A plastic mesh was placed between the anode and cathode to prevent contact. The electrolyte was a phosphate buffer solution (PBS) containing ∼1 g/L glucose \(^{S2}\). The MB was operated with a fixed current output, controlled by a Bio-Logic VMP3 potentiostat-galvanostat. For the plate-shaped MB used to investigate the charge efficiency and energy efficiency of the MB, the operation was stopped when the cell voltage dropped to 0 V. At this point, the electrolyte before and after the operation cycle...
was analyzed. The bottle-shaped MB was applied to study operational parameters and the cycling performance of PB electrodes, where a double junction Ag|AgCl|KCl reference electrode (RE) was placed in the MB. The operation was stopped at designated cut-off potentials for the PB electrode.

**Characterization.** A BioLogic VMP3 potentiostat-galvanostat was used for all electrochemical characterizations. A double junction Ag|AgCl|KCl reference electrode (RE) and a Pt counter electrode (CE) were used as needed. X-ray diffraction measurements (XRDs) were carried out with a PANalytical X’Pert (Ni-filtered Cu Kα radiation). Scanning electron microscope (SEM) images were obtained with a FEI Nova NanoSEM. For the SEM, the anode sample was pretreated with a fixing and critical point drying process $^{S2}$. The chemical oxygen demand (COD) of the electrolyte was determined using a HACH COD analysis kit (HACH, Co., USA).

**References**

Supplementary Figures

Fig. S1. X-ray diffraction (XRD) patterns of the PB electrodes as-prepared and after 20 cycles of reduction-and-regeneration operation in a MB.

Fig. S2. Potential of the pre-cultured carbon cloth microbial anode (3 cm × 3 cm) at different current outputs. The current output values are labeled above the potential curve.
Fig. S3. Scanning electron microscope (SEM) image of the PB electrodes after 20 cycles of reduction-and-regeneration operation in an MB.