Supplementary Information

Biorefinery of Galacturonic Acid Using a Biofuel Cell as a Reactor

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Figure S1 Amperometric I-t curves for a PMG modified CF electrode. Measurements under conditions with enzyme and substrate (black), substrate and no enzyme (red), and enzyme and no substrate (blue).



Figure S2 CVs of the PQQ-GDH / PMG / PFC anode (magenta) and the BOD / PFC cathode (green) in 0.1 mol dm⁻³ phosphate buffer (pH 7.0) containing 0.1 mol dm⁻³ galacturonate under O_2 atmosphere at a rate of 2 mV s⁻¹. Plastic formed carbon (PFC<mark>, 3 mm diameter</mark>) electrodes were used as base electrodes instead of CF electrodes. Dotted CVs are the results of control experiments. CV of the anode (magenta) in 0.1 mol dm⁻³ phosphate buffer (pH 7.0) without galacturonate and CV of the cathode (green) in 0.1 m phosphate buffer (pH 7.0) with 0.1 mol dm⁻³ galacturonate under N₂ atmosphere.



Figure S3 The polarization curve (black) and power curve (red) of the EBFC obtained by LSV (vs. Ag/AgCl reference) under O_2 bubbling (0.8 L/min). The voltage was swept from the OCV to 0 V at a rate of 2 mV s⁻¹. The electrolyte solution was 0.1 mol dm⁻³ galacturonic acid/buffer (7 mL). Carbon felt with a diameter of 10 mm and a thickness of 5 mm was used to prepare the electrodes. The anode consisted of PMG-CF modified with PQQ-GDH. The cathode consisted of bare CF modified with BOD.



Figure S4 The polarization curve (black) and power curve (red) of the EBFC using glucose as a substrate.



Figure S5 The polarization curves (dotted lines) and power curves (solid lines) of the EBFCs with a Nafion membrane (red) and without membrane (black).



Figure S6 Results obtained from a discharge experiment of the BFC using a 5-k Ω external resistance. O₂ (0.3 L/min) was bubbled through the reaction solution 5 minutes before, but not during, measurement. The electrolyte solution was a 0.1 mol dm⁻³ galacturonic acid/deuterated buffer (7 mL). (a) *I-t* curve and (b) *V-t* curve of the cathode (black) and anode (red) vs. an Ag/AgCl reference. Carbon felt with a diameter of 10 mm and a thickness of 5 mm was used to prepare the electrodes. The anode was PMG-CF modified with PQQ-GDH. The cathode was bare CF modified with BOD.



Figure S7 V-t curve of the cathode (red) without BOD, anode without PQQ-GDH (blue), and cell (black). All conditions are the same as in Fig. 5 except for the absence of enzyme on both electrodes.



Figure S8 Calibration curve of galactaric acid generated using NMR. The measurement solution was prepared by dissolving galactaric acid (0.29 mg, 0.53 mg) in 500 μ L of a deuterated buffer and adding DSS (0.5 mg/5 μ L). The integrated intensity of the 3.95 ppm peak of galactaric acid (a3,4) was calculated using an integrated intensity of 1 for the 0 ppm peak of DSS.



Figure S9 (a) *V-t* curve measured without a load resistance under O_2 bubbling (0.9 L/min). The changes in the potentials of the cathode (black) and anode (red) vs. an Ag/AgCl reference are shown. (b) The NMR spectrum obtained for the reaction solution after a 24-h period. The relative integrated intensity of the a3,4 peak (red arrow) is 0.13 for an integrated intensity of 1 for the 0 ppm peak of DSS and is used in conjunction with the calibration curve shown in Figure S8 to yield 0.24 mg of galactaric acid in 500 µL. The electrolyte solution was a 0.1 mol dm⁻³ galacturonic acid/deuterated buffer (7 mL). Carbon felt with a diameter of 10 mm and a thickness of 5 mm was used to prepare the electrodes. The anode was PMG-CF modified with PQQ-GDH. The cathode was bare CF modified with BOD.