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Supporting Information

Tailoring Microbial Electrochemical Cells for Production of Hydrogen Peroxide at High Concentrations and Efficiencies

Michelle N. Young,*[a] Mikaela J. Links,[a] Sudeep C. Popat,[a, b] Bruce E. Rittmann,[a] and César I. Torres*[a]

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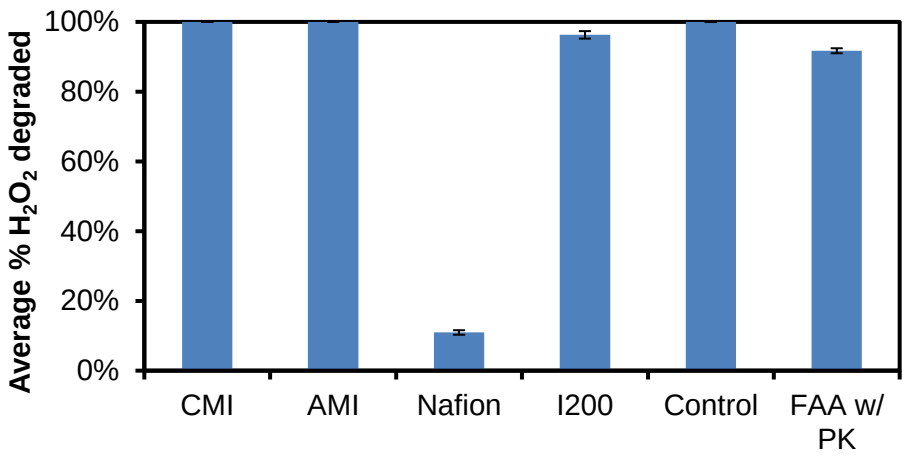
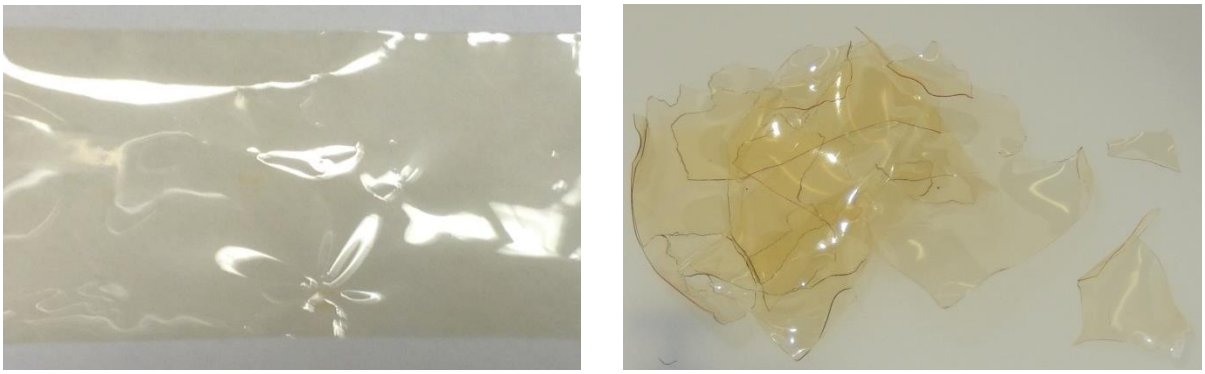
A. Supplemental Graphs

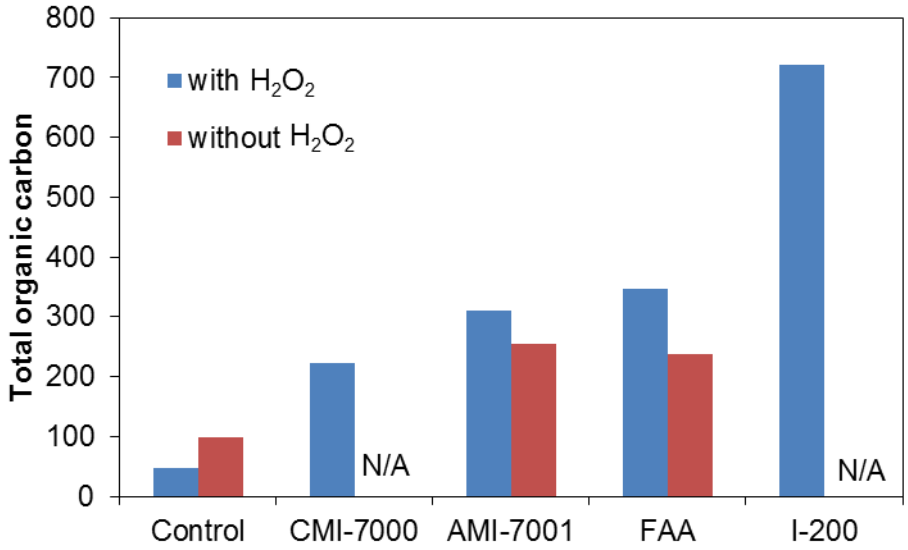


SI Figure 1. H_2O_2 degraded during batch bottle tests for membrane stabilities at pH 12.

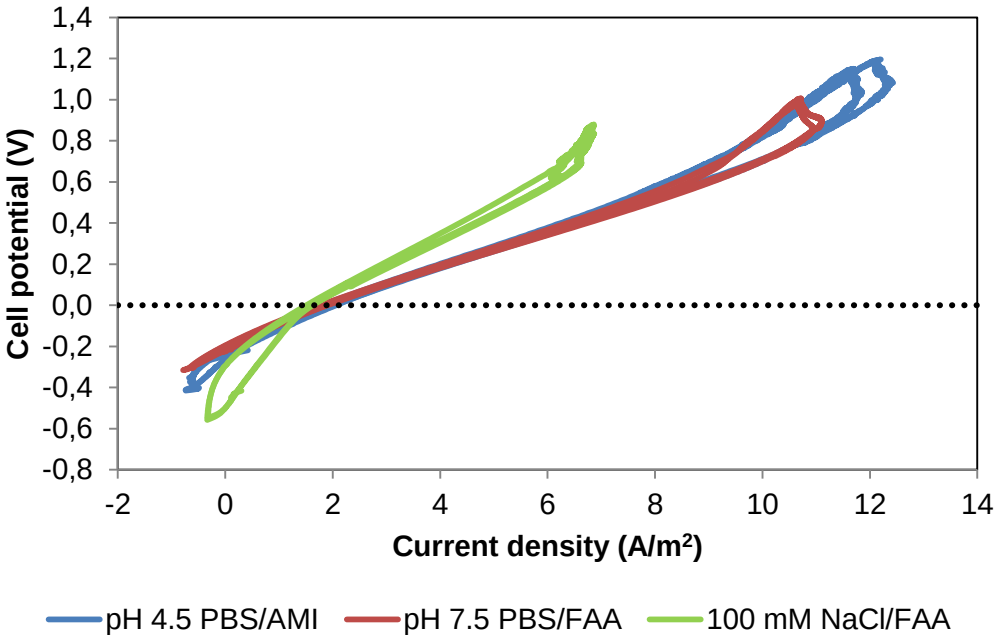


(a) (b)

SI Figure 2. FAA (a) before and (b) after pH 12 100-mM NaCl and 1% H_2O_2 stability tests. The stability tests used a 3 cm x 3 cm square that deteriorated to pieces by the end of the 45-day test.



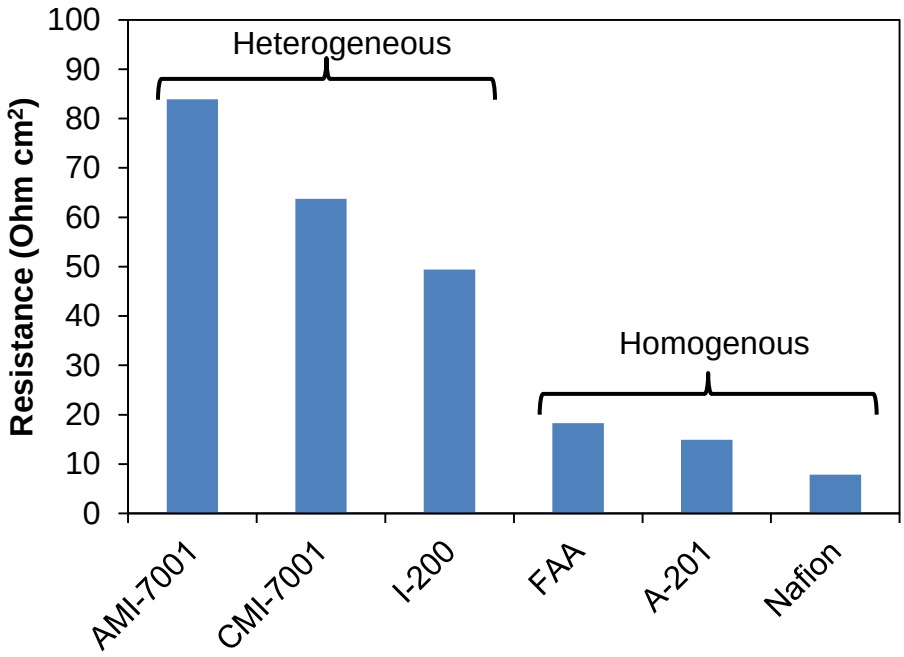
SI Figure 3. Total organic carbon (TOC) from batch bottle tests of membrane stabilities with and without 1% H_2O_2 present in the solution at pH 12. TOC measurements were obtained using a Shimadzu TOC-V CSH Total Organic Carbon analyzer. Tests were not performed on CMI-7000 and I-200 at pH 12 only.



SI Figure 4. CVs of preliminary reactor design. The PP-MEC CVs were performed with two different membranes (FAA and AMI-7001) and three different catholytes: 100 mM NaCl, pH 4.5 PBS, and pH 7.5 PBS. The PP cell was operated at a 4 hr HRT and 30 cm^3/min air flow rate. The reactor design was the same as the reactor presented in this paper, except there was 1 cm distance between the anode and cathode. The FAA membrane is ~1/3 the thickness of the AMI membrane and has a lower resistance.

B. EIS characterization of membrane resistances

We tested the membranes in a 100-mM $NaHCO_3$ solution using electrochemical impedance spectroscopy (EIS) to determine their ionic transport resistances. EIS was performed at 100 kHz and 10 mV amplitude with the anode as the working electrode and the cathode as the counter electrode. As illustrated in SI Figure 5, heterogeneous membranes exhibited 45-85 ohm-cm^2 in resistance. Homogeneous membranes demonstrated resistances <20 ohm-cm^2. For perspective, at 10 A/m^2, the homogeneous membranes have Ohmic overpotential <20 mV and heterogeneous membranes between 50-85 mV.

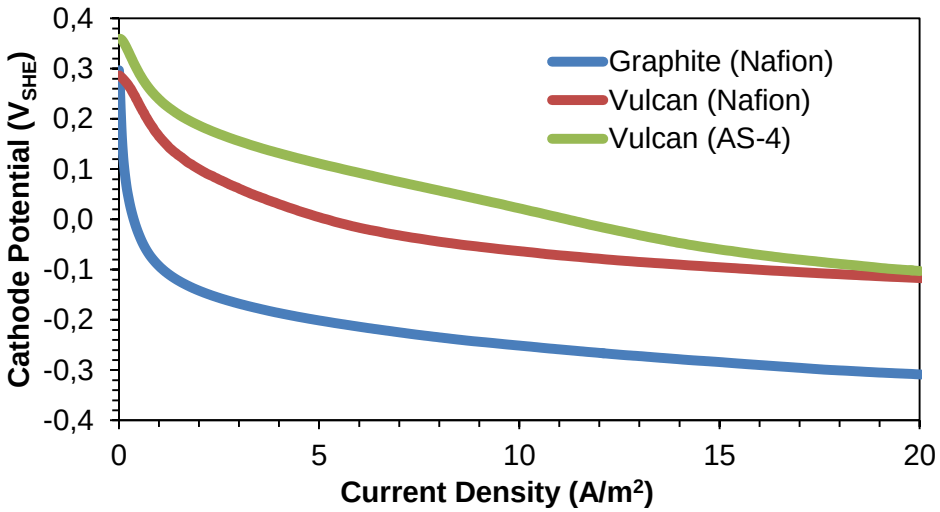


SI Figure 5. Area-specific resistances determined using electrochemical impedance spectroscopy for seven different heterogeneous and homogenous membranes in 100 mM $NaHCO_3$.

C. Linear Sweep Voltammetry to Determine Activation Overpotentials in Catalyst/Binder Combinations

We used gas-diffusion half-cells to evaluate differences between catalyst and binder performance. We evaluated three catalyst/binder combinations: 50 g/L Vulcan carbon (FuelCellStore.com) in a 5% cationomer Nafion solution (10% Nafion in alcohol, Sigma-Aldrich); 62.5 g/L of Vulcan carbon in an 3.13% anionmer AS-4 solution (5% AS-4 in alcohol, Tokuyama Corp.); and 87.7 g/L of graphite (Sigma-Aldrich) in a 8.77% Nafion solution. The catalyst/binder was coated on a 9-cm^2 hydrophobic carbon cloth (FuelCell.com) at a loading of 0.5 mg/cm^2 and dried for 24 h. The cathode and a 316-stainless steel rod anode were placed in a 27 mL half-cell filled with 100-mM sodium perchlorate solution (Popat et al. 2014). A standard calomel electrode (SCE, CH Instruments, Inc.) was used as the reference (+0.21 V_{SHE}). For experiments utilizing NaOH or H_2O_2 in solution at the start, we used a Nafion-117 membrane to separate the cathode and anode chambers. The catalysts/binders were evaluated using linear sweep voltammetry (LSV) between -0.19 and 0.61 V_{SHE} at 1 or 2 mV/s scan rate and 30°C.

As illustrated in SI Figure 6, the negatively-charged OH^- and HO_2^- produced at high pHs are more effectively transported from the cathode surface using the anionic AS-4 binder, resulting in lower concentration overpotential versus the cationic Nafion binder. Membrane-stability tests (not presented here) demonstrated that anionic polymers like AS-4 are not stable with H_2O_2, especially at high pH, eliminating it as a potential binder.



SI Figure 6. Cathode potentials (up to 20 A m^{-2}) established using linear sweep voltammetry with three catalyst/binder combinations: 50 g/L Vulcan carbon in a 5% Nafion solution (labeled Vulcan (Nafion)); 62.5 g/L of Vulcan carbon in an 3.13% AS-4 solution (labeled Vulcan (AS-4)); and 87.7 g/L of graphite in a 8.77% Nafion solution (labeled Graphite (Nafion)).