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Capacitive Mixing Power Production from Salinity Gradient Energy Enhanced through Exoelectrogen-Generated Ionic Currents

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1. Increased ion transport to capacitive electrodes

Ion transport is dictated by the Nernst-Planck-Poisson (NPP) model. Thus, the ion flux is due to ion concentration gradients (diffusion) and potential gradients (electromigration). Previous capacitive deionization models (the opposite process to CapMix) have described a simplified approach to calculate these fluxes[34]. The transport of ions due to the electrostatic driving forces is calculated through

$$J_{charge} = k \cdot c \cdot \Delta\phi_{mtl} \qquad \text{(Eq. 1s)}$$

where J_{charge} is the ion flux (mol m^{-2} s^{-1}), k is the mass transfer coefficient, c is the ion concentration in the solution, and $\Delta\phi_{mtl}$ voltage gradient divided by the thermal voltage (V_T=RT F^{-1}). Likewise, ion transport in an electrochemical system such as the MFC can be estimated if the current passing through the external circuit is known as:

$$J_{cur} = \frac{i}{AnF} \qquad \text{(Eq. 2s)}$$

where J_{cur} is the ionic current induced by the electrical current (i), A is the cross sectional area, n is the (mol e^- · mol^{-1}), and F is faradays constant. Thus, for a pure CDP process, the flux of ions may be dictated by J_{charge}, and for the CMFC flux is approximated by J_{charge}+J_{cur} (Fig 5s).

While this approximation for electromigration plays a significant role in the enhanced voltage, concentration gradients also may be important. For CDP, while there is no need for an external power supply, the voltage window remains limited by the membrane potential which is a function of the concentration gradient across the membrane

$$\Delta\phi_{mem} = \ln\left(\frac{c_{sp}}{c_e}\right) \qquad \text{(Eq. 3s)}$$

where c_{sp} is the concentration in the spacer, and c_e is the concentration in the electrode. Based on equation 5, slight changes in the high and low concentrate in either the spacer or electrode can significantly reduce the established membrane potential (Fig 6s). Because the voltage window is inherently small, obtaining the theoretically maximum voltage is necessary for useful energy extraction, and thus establishing concentration gradients across the membrane quickly is important. Previous theoretical work showed that in practice the observed voltages can be 50% less than the theoretical limit [9]. This reduction was attributed in part to charge leakage, and to insufficient flow at the electrode/spacer interface which reduced the concentration difference. Thus, another reason for the enhanced voltages from the capacitive electrodes produced in the MFC may be due to the creation of a rapidly established concentration gradient across the membrane.

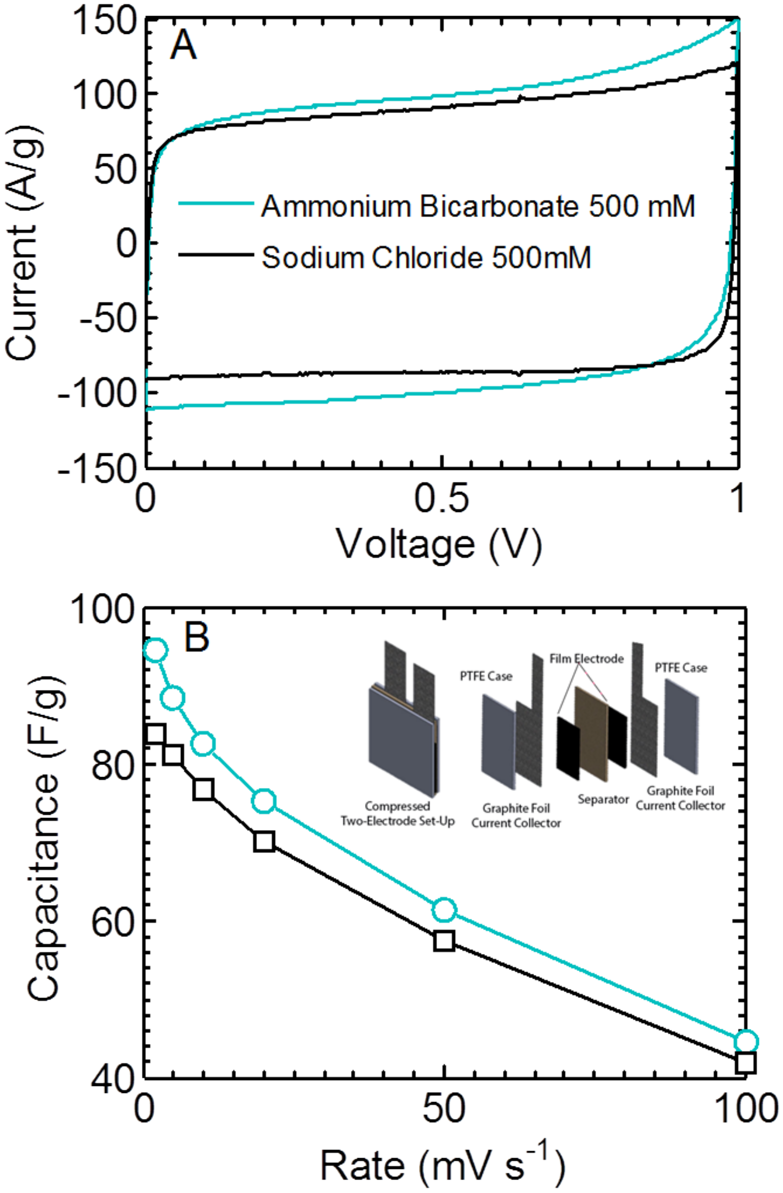

Fig. 1s: (a) Cyclic voltammetry of film electrodes within high concentration (500 mM) sodium chloride and ammonium bicarbonate solutions (b) Capacitance versus scan rate obtained from cyclic voltammetry at various scan rates with inset displaying the two electrode assembly used.

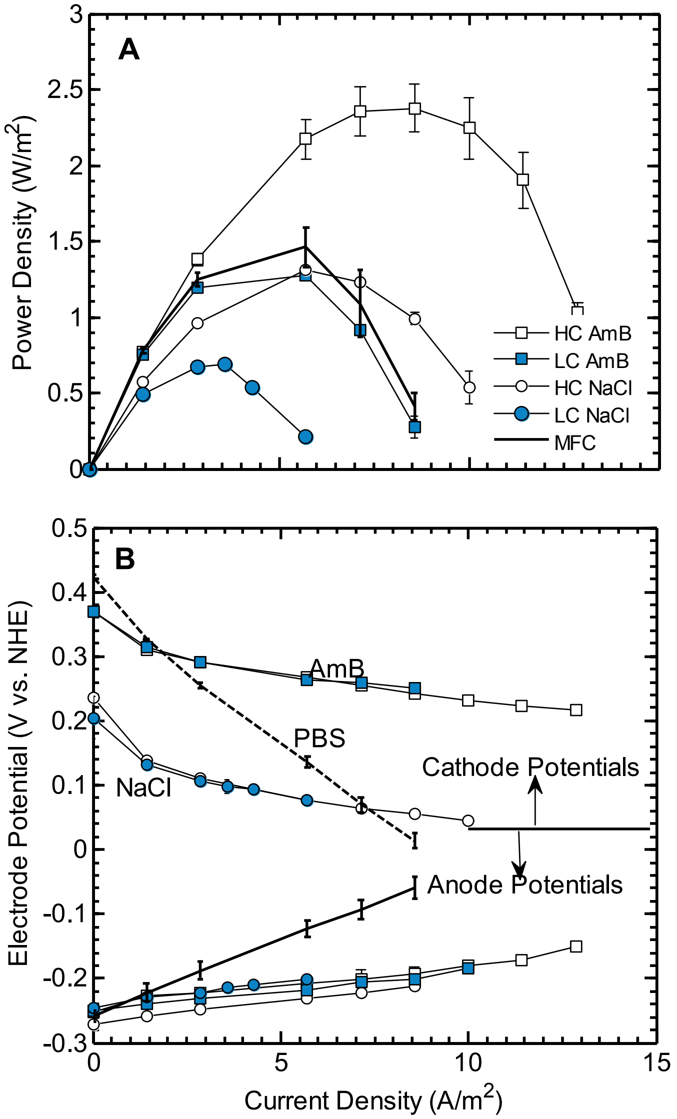

Fig. 2s: Steady state whole cell power density for three chamber microbial fuel capacitive mixing system when CapMix chamber contains high and low concentration solutions and (b) individual electrode potentials.

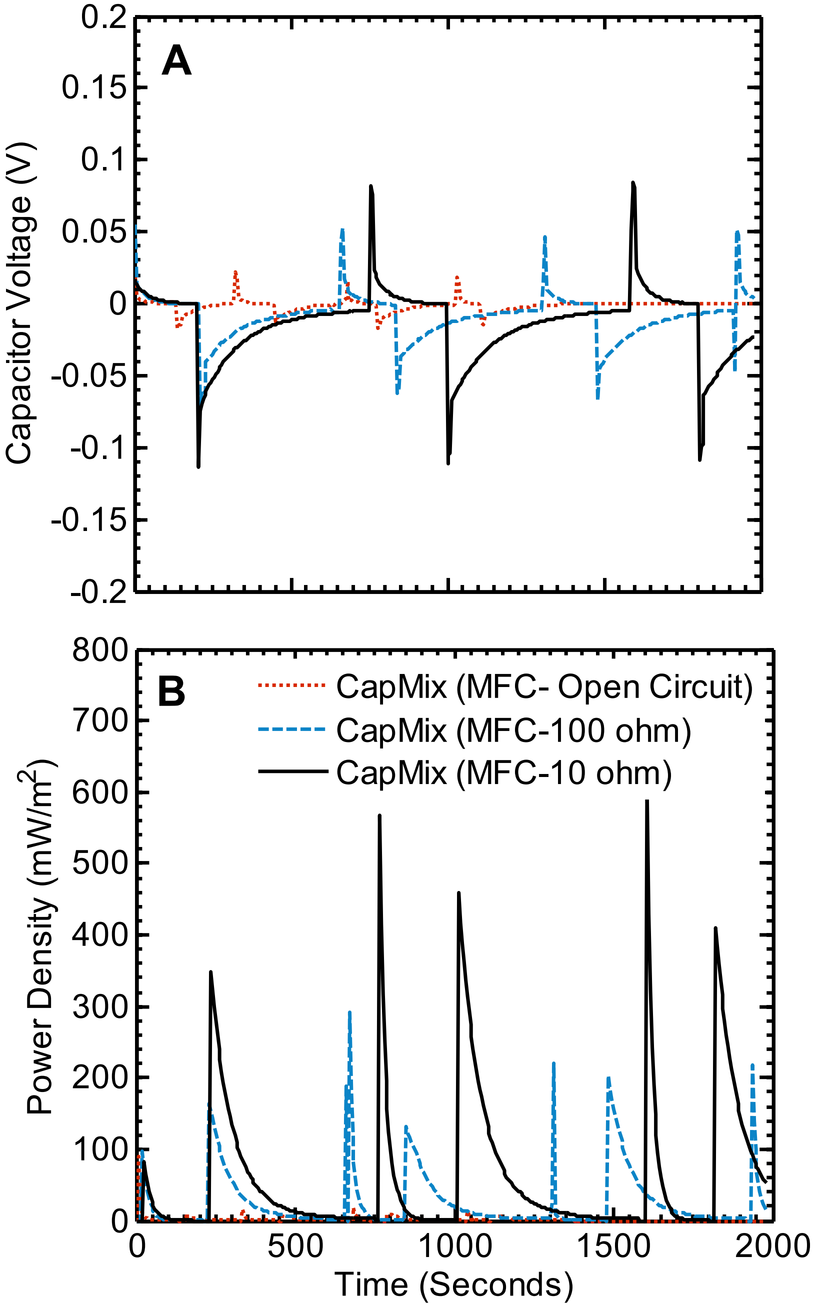

Fig. 3s: Potential and power density over successive cycles with MFC operated under constant load (resistance) conditions.

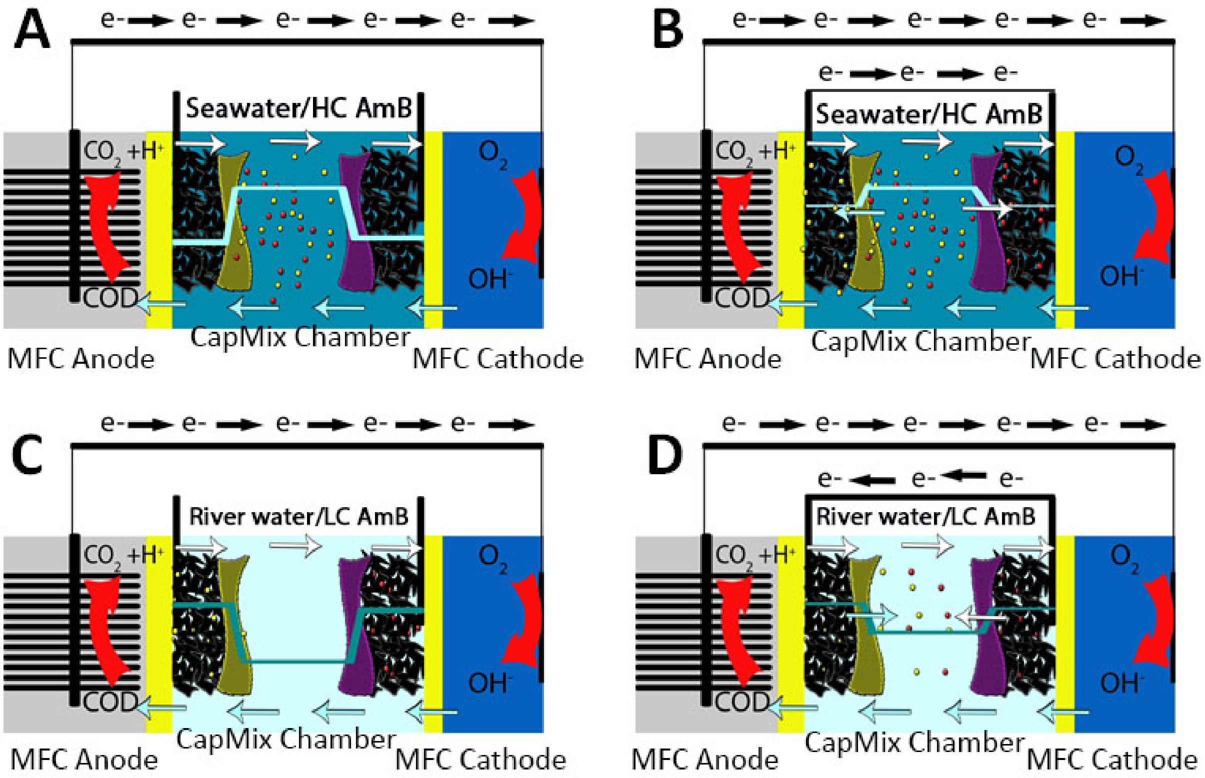

Fig. 4s: CMFC system (not drawn to scale) with MFC electrodes in a constant state of discharge and CapMix chamber undergoing the four step process for energy extraction. Ion fluxes are indicated by blue and white arrows.

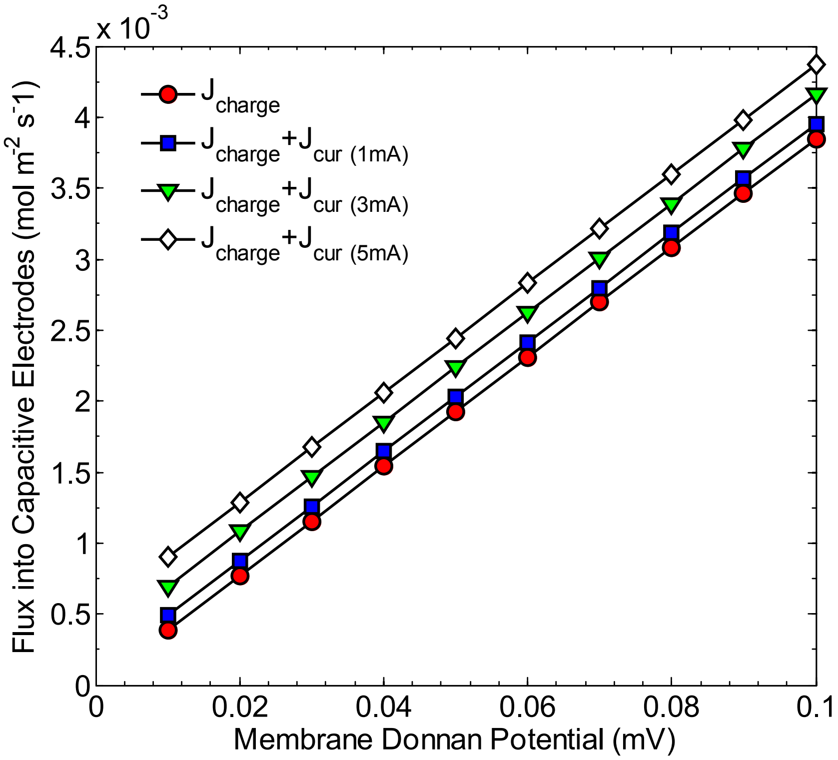

Fig. 5s: Evaluation of flux into capacitive electrodes as result of a generated Donnan (membrane) potential and ionic currents induced by the MFC.

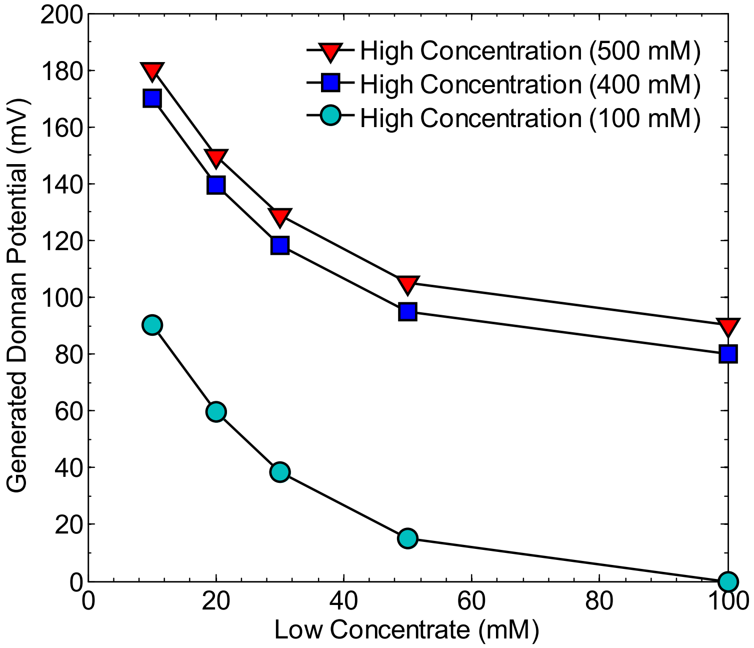

Fig. 6s: Donnan (membrane) potential generated with various high and low concentration NaCl solutions.

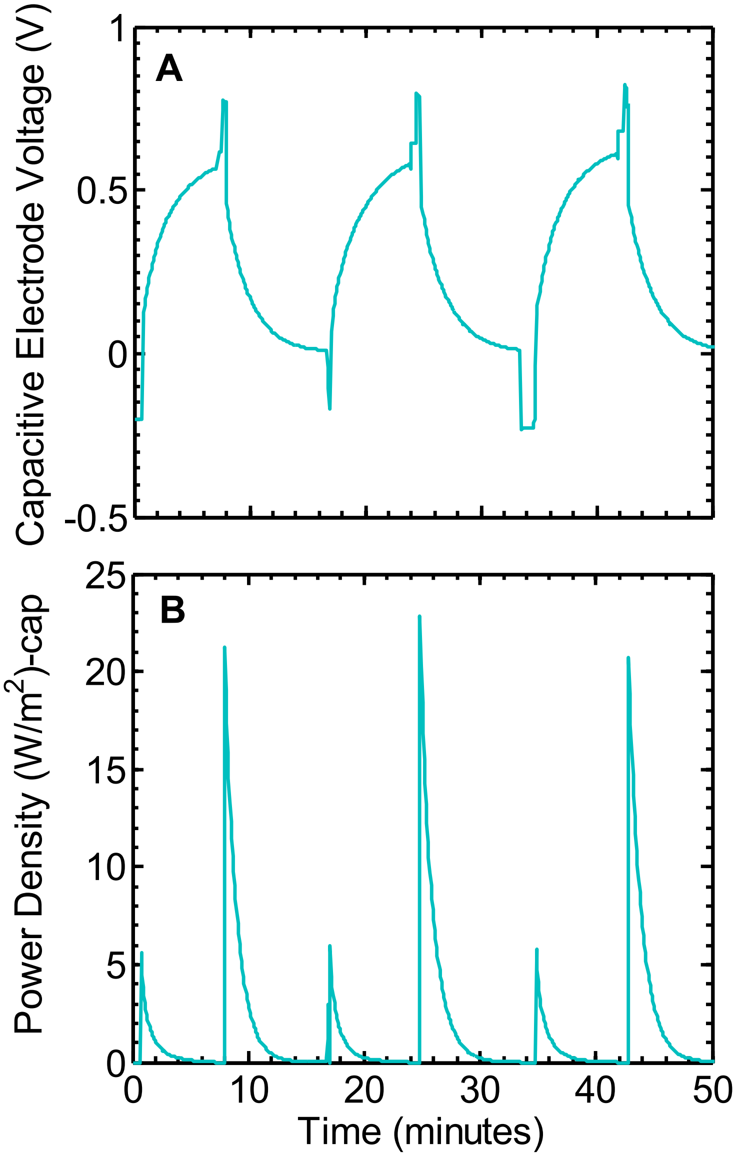

Fig. 7s: Forced charge from MFC performance data (discharge through 100 ohm resistance) (a) capacitor voltage and (b) power densities.

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Table 1s: Capacitive mixing performance values from literature

Year	**Source**	**CapMix Process**	**Peak Discharge Power Density (mW m-^{2})**	**Energy Per Cycle (mJ cyle^{-1})**	**Energy Per Cycle (J cyle^{-1} m^{-2})**	**Energy Per Cycle (mJ cyle^{-1} g^{-1})**
2009	(8)	CDLE	NR	0.005	0.398	12.5
2010	(9)	CDP	40	400	13.89	50.0
2011	(15)	CDLE	18	2000	69.444	250
2011	(7)	Battery Mixing	105	29.5	295	NR
2012	(7)	Battery Mixing	138	38.2	382	NR
2012	(16)	Forced CDP	200*	641	80	493
2012	(14)	CDLE	50	NR	NR	NR
2013	This Study	MFC-CDP (AmB)	942	5.2	52	314
2013	This Study	Forced MFC-CDP (AmB)	7000-21000	223	2230	14867

*Denotes average peak power density

Shaded rows denote processes which required input energy

NR – Values Not Reported

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