Capacitive mixing power production from salinity gradient energy enhanced through exoelectronically generated ionic currents†

Marta C. Hatzell,a Roland D. Cusickbc and Bruce E. Logan*b

Several approaches to generate electrical power directly from salinity gradient energy using capacitive electrodes have recently been developed, but power densities have remained low. By immersing the capacitive electrodes in ionic fields generated by exoelectrogenic microorganisms in bioelectrochemical reactors, we found that energy capture using synthetic river and seawater could be increased ~65 times, and power generation ~46 times. Favorable electrochemical reactions due to microbial oxidation of organic matter, coupled to oxygen reduction at the cathode, created an ionic flow field that enabled more effective passive charging of the capacitive electrodes and higher energy capture. This ionic-based approach is not limited to the use of river water-seawater solutions. It can also be applied in industrial settings, as demonstrated using thermolytic solutions that can be used to capture waste heat energy as salinity gradient energy. Forced charging of the capacitive electrodes, using energy generated by the bioelectrochemical system and a thermolytic solution, further increased the maximum power density to 7 W m⁻² (capacitive electrode).

Broader context

There is currently an enormous amount of free energy released through the mixing of river and seawater at estuaries. Furthermore, an abundance of untapped energy is also known to reside within organic matter present in many wastewaters. With a growing emphasis placed on mitigating the dependence between our expanding water and energy infrastructures across the globe, the development of sustainable dual energy generation and water treatment process is highly desirable. A combined capacitive mixing – bioelectrochemical system could not only harvest this energy, but ultimately provide a new means for energy generation and wastewater treatment.

Introduction

Harnessing the entropic energy released when river water and seawater mix could globally provide ~1 terawatt of renewable power. To capture this energy, three main processes have been used: pressure retarded osmosis (PRO), reverse electrodialysis (RED), and capacitive mixing (CapMix). These three processes are based on reversing three common approaches used to desalinate water, which are reverse osmosis, electrodialysis, and capacitive deionization. Industrial scale PRO and RED applications have been limited primarily due to relatively high energy requirements for river water and seawater pretreatment, high costs of membranes, and reduced lifetimes due to fouling. The CapMix approach to extract salinity gradient energy is based on controlled ion transfer to and from capacitive or battery electrodes. Suitable materials for energy generation using battery electrodes have not sufficiently advanced as precious metals (e.g. Ag) can be required. In contrast, capacitive electrodes can be made from materials that are both renewable and inexpensive (such as activated carbon), and they can have longer lifetimes than battery electrodes.

CapMix energy is captured by cycles of charging and discharging capacitive electrodes with seawater and river water. The energy can be captured with these capacitive electrodes two different ways: either through changes in membrane potentials due to ion concentration gradients, or through work done by expansion of the electric double layer. For energy recovery based on changes in the membrane potentials (also called Donnan potentials), the capacitive electrodes are coated with ion exchange polymers that allow only selective charge transfer (anions or cations) to each of the electrodes. Energy captured using this capacitive Donnan potential (CDP) approach requires cycles that consist of four separate steps (Fig. 1a). Initially,
under open circuit conditions, the capacitive electrodes are polarized using a high concentrate solution (seawater) due to the generation of a membrane potential at each electrode (Step 1). Next, the capacitive electrodes are connected to an external load which allows the flow of electrical current through a circuit, and ionic current in the electrolyte (Step 2). Once the capacitive electrodes are fully charged (voltage \( U = 0 \)), the circuit is again opened (no current) and a low concentrate solution (river water) is introduced, reversing the polarity of each membrane potential (Step 3). The electrodes are then connected to an external load and discharged, creating an electrical current in the opposite direction (Step 4). The net energy that is extracted is defined by the voltage window produced by the membrane potential (Fig. 1b). This four step CDP cycle results in spontaneous energy generation, and therefore the process does not require any electrical input energy. However, the potential energy, \( E \), that can be recovered is limited as only a relatively small voltage (<100 mV) can be produced by the membrane potential alone \( (E = 1/2CU^2) \), where \( U \) is the voltage, and \( C \) is the capacitance).

To increase the amount of energy recovered from this four step cycle, an external power supply is used in Step 2 to increase the charge loaded onto the membrane-coated electrodes (called forced CDP) (see Fig. 1b). While the use of the power source requires additional energy to be put into the system, the forced charging step increases the size of the voltage window. As long as there is no substantial charge leakage (i.e. coulombic losses during the charging step), the current extracted in Step 4 (at a higher voltage) enables increased energy recovery, as shown by the larger voltage window (Fig. 1b). Thus, the peak power density that can be obtained using forced CDP has been increased to an average of 200 mW per square meter of electrode area,\(^{14} \) compared to 20–40 mW m\(^{-2} \) using (passive) CDP.\(^{9,11} \) However, even these higher power densities for forced CDP are still well below those reported for RED (0.95–1.2 W m\(^{-2} \) membrane area)\(^{15,16} \) or PRO (1–10 W m\(^{-2} \) membrane area).\(^{17,18} \) Thus, this technology will not be useful for energy generation until power densities can be substantially improved.

One approach recently used to increase energy recovery from salinity gradients using RED was incorporating the RED stack of membranes into a bioelectrochemical system, such as a microbial fuel cell (MFC). The combination of these two technologies enabled significant improvements in performance for both technologies.\(^{19–21} \) The RED process was improved because the reactions at the MFC electrodes were thermodynamically favorable, thereby avoiding energy losses needed to overcome unfavorable reactions usually occurring with RED alone. The MFC process was improved due to the reduced electrode overpotentials that resulted from the ionic current that was driven by the RED stack.\(^{20,22} \) The combination of these two technologies thus created a more effective means to harvest both free energy associated with the salinity gradients, as well as energy in a domestic wastewater (1–2 kWh per m\(^3 \) of wastewater)\(^{23} \). The success in combining salinity gradient and bioelectrochemical technologies suggested that it might be possible to improve performance of the other salinity gradient energy technologies by using MFCs.

A new method was developed here to increase CDP performance by placing the capacitive electrodes into the ionic field generated in a galvanostatically driven bioelectrochemical system (BES) (Fig. 2a). When exoelectrogenic bacteria oxidize organic matter and release electrons to the anode in a BES such as an MFC, ions (protons) are released into the electrolyte, and protons are consumed at the cathode.\(^{24} \) In order to maintain electroneutrality, an electric field drives ionic currents in the
solution either through the motion of protons or by transport of other ionic species.\textsuperscript{19,20,25} It was reasoned that immersion of capacitive electrodes into this ionic field could enhance charging of these capacitive electrodes, and enable increased power densities through the CapMix process. The combined process could then be used capture energy both from salinity gradients and organic matter in wastewater with the BES.

The energy and power produced from both the CDP, and combined CDP-BES process, was examined here to show that the process could improve the CapMix process. In addition to tests using synthetic seawater and river water solutions (NaCl), the use of recyclable thermolytic salts (ammonium bicarbonate, AmB) was also examined. Capacitive energy extraction so far has only been investigated using NaCl solutions, which would limit applications to coastal regions. The use of thermolytic solutions enables closed loop operation using waste heat, with conventional distillation processes for solution regeneration. Industrial waste heat accounts for between 20 and 50% of industrial energy input,\textsuperscript{26} and capturing this energy using AmB would allow for power generation at industrial sites where it could readily be used. Both conventional CDP and forced CDP processes were investigated for improving performance of CapMix systems with AmB and NaCl solutions.

Materials and methods

Capacitive mixing bioelectrochemical system design

The combined CapMix and BES system, called a capacitive mixing bioelectrochemical system (CBES), consisted of three chambers: anolyte, CapMix, and catholyte (Fig. 2a). The three chambers were separated from each other using two anion exchange membranes (AEMs). The use of the membranes allowed the solutions used for the two different processes to remain separated, while maintaining an ionic connection needed for the BES. The anolyte chamber was created from a 4 cm polycarbonate cube which had a 28 mL cylindrical chamber cut out. The CapMix (middle chamber) and catholyte chambers consisted of a 2 cm polycarbonate cube, each 14 mL with the same diameter cylindrical chambers. Brush anodes (manufactured by Mill-Rose, Mentor, OH) were made from graphite fibers twisted between two titanium wires (4 cm diameter). Anodes were heat treated and enriched in a vertical configuration within single chamber MFCs, as previously described (26). When enrichment was complete the anode was transferred to the CBES anolyte chamber. The anolyte solution used in all tests was a 50 mM phosphate buffer, 1 g l\textsuperscript{-1} sodium acetate and trace vitamins and minerals.\textsuperscript{27}

Cathodes were made using wet proofed carbon cloth (type B, E-TeK) which was coated with carbon black, platinum (0.5 mgPt cm\textsuperscript{-2}) and a NAFION\textsuperscript{®} 117 (Aldrich) binder on the water side.\textsuperscript{27} The air side had 4 layers of polytetrafluoroethylene (PTFE) coatings which acted as diffusion layers to allow oxygen diffusion to the catalyst, and to prevent water leakage.\textsuperscript{28} The catholyte solution consisted of the high concentrate saline solution, which was either 500 mM NaCl or NH\textsubscript{4}HCO\textsubscript{3} as indicated.

The capacitive electrodes were made using 90 wt% YP-50F activated carbon (Kuraray Chemical Company, USA), 5 wt% polytetrafluoroethylene as a binder, and 5 wt% carbon black (100% compressed; Alfa Aesar, USA) to increase electrode electrical conductivity. The resultant slurry was rolled and cut into square electrodes with an area of 1 cm\textsuperscript{2} and an approximate weight of 15 mg. During electrochemical characterization tests, the electrodes were placed on non-corrosive current collectors made of graphite foil. A polyvinylidene fluoride (PVDF) membrane with a mesh width of 100 nm (Durapore®; Merck Millipore, Germany) was used as the separator between the two electrodes. The entire cell was compressed between two PTFE plates with clips.

For CapMix tests the capacitive electrodes were hot pressed onto a current collector (SS mesh Type 316, McMaster-Carr). One coating of an anion exchange polymer (polysulfone polymer with quaternary ammonium groups)\textsuperscript{29} was put onto one capacitive film electrode, and one coating of cation exchange polymer (NAFION\textsuperscript{®} 117) polymer was put onto the other one. Both electrode were dried overnight prior to use. These capacitive electrodes were placed on either side of the central CapMix chamber (2 cm apart). The capacitive electrode with the anion coating was placed against the AEM membrane–anolyte interface, with the membrane coated capacitive electrode side facing the water side. The capacitive electrode with the cation coating was placed near the membrane–catholyte interface, with the membrane coated facing the water side of the CapMix chamber.

Ex situ capacitive electrode electrochemical characterization

The capacitive electrodes were electrochemically characterized in a symmetrical two electrode set-up (Fig. 1s). Cyclic voltammetry (CV) studies of the capacitive electrodes were performed using this two-electrode setup as previously described.\textsuperscript{30,31} CVs were run at different scan rates (2, 5, 10, 20, 50, 100 mV s\textsuperscript{-1}) in the different aqueous media used here to assess their performance (Fig. 1s). From these CVs, the specific gravimetric \(C_{sp}\) was obtained using
where $\Delta U$ is the width of the voltage scan, $i$ is the discharge current, $U$ is the voltage, $v$ is the scan rate, and $m$ is the mass of carbon in one electrode.

### Capacitive mixing performance

The CapMix (middle chamber) and BES (end chambers) were operated separately without any electrical connections between the two systems (Fig. 2). The BES was operated by connecting the brush anode to the air breathing oxygen reduction cathode through an external load (controlled by the galvanostat). Likewise, the two capacitive electrodes within the CapMix chamber were connected to each other through a separate external load. Energy obtained through the BES circuit was due to the oxidation of organic matter (acetate), while energy harvested through the CapMix circuit was due to mixing energy.

The BES was operated under constant current conditions between 1 and 5 mA (galvanostatically), which was chosen to ensure that the BES potential was positive when either the high or low concentration solution was present within the CapMix chamber. Separate tests using a constant load (resistor) were also conducted to demonstrate that the use of the galvanostatic operation for these tests did not produce different results than those under typical BES operation with a constant load (Fig. 3A† and 3). Substrate removal in the BES was not monitored. While the BES electrodes were maintained in a constant discharge mode using the galvanostat, the capacitive electrodes were repeatedly cycled through the four step CDP energy extraction process. Briefly, in Step 1, capacitive electrodes were polarized in the high concentration solution (NaCl or AmB) under open circuit conditions (Fig. 4A†). In Step 2 the capacitive electrodes were connected to a 10 Ω external resistance for 5 minutes, until the current through the circuit approached zero (Fig. 4B†). In Step 3, the capacitive electrodes were again disconnected (open circuit), and the low concentration solution was replaced by the low concentration solution (10 mM NaCl or AmB) (Fig. 4C†). After the electrode polarity switched due to the reversal of the membrane potential, in Step 4 the capacitive electrodes were discharged through a 100 Ω resistor for 20 minutes (Fig. 4D†). This cycle was repeated 5–10 times to ensure repeatability.

### Forced capacitive mixing performance

Forced charge CDP experiments were conducted using the BES as the power source. All forced charge CDP tests used 500 mM and 10 mM AmB as the high and low concentrate solutions in the CapMix chamber, and 500 mM AmB as the catholyte in the BES. The same four step process described for CDP operation was used (Fig. 1a), except that during Step 2 the BES electrodes were connected to the capacitive electrodes through a connecting wire (Fig. 1b). The BES electrodes were connected to the capacitors for 5 minutes, and current was monitored by measuring the voltage drop across a 10 Ω resistor. Next, the BES and capacitive electrodes were disconnected and the CapMix chamber was flushed with the low concentrate solution, reversing the membrane potential (Step 3). The capacitive
electrodes were then discharged through an 800 Ω resistor for 1 hour to reduce the charge leakage (Step 4). During this time, the BES electrodes were connected to a 10 Ω resistor. After 1 hour, the capacitors were left in open circuit, and the low concentrate was replaced with a high concentrate. The cycle was repeated multiple times to ensure repeatability.

Results and discussion

Evaluating the effect of BES current on CapMix

To demonstrate enhancement on CapMix by BES ionic currents, the capacitive electrodes were cycled multiple times through the four-step energy extraction process with the BES current set at 2 or 4 mA using NaCl solutions. The capacitive electrodes were charged for five minutes (10 Ω external resistance) in high concentration solution, and discharged for 20 minutes (100 Ω resistor) in low concentration solution. At 2 mA, the peak voltage was 114 ± 4 mV (n = 3), producing a maximum power density of 232 ± 18 mW m⁻² (average of 44 ± 4 mW m⁻²) (Fig. 3). This is a 2.3× increase in voltage, and 24× increase in maximum power compared to controls with no enhanced ionic current (35 ± 0 mV and 9.6 ± 0.3 mW m⁻²; average of 0.013 ± 0.001 mW m⁻², n = 4). The low power density for the capacitive electrodes in the absence of the ionic current was consistent with previous reports (Table 1s†). When the BES current was increased toward the limiting current that could be produced by this reactor (~4 mA), the peak power increased to 448 ± 67 mW m⁻² (77 ± 24 mW m⁻² average), which was 11× more power than that previously obtained in CDP tests (no forced charging), and 46× that achieved with the same capacitive electrodes and no induced ionic current (Table 1s†). Multiple CapMix cycles were possible because the length for a full CapMix cycle (~30 min) was substantially less than that needed for a single BES fed-batch cycle (16–18 h). A higher current might have further increased power densities produced by the CDP, but this was not possible with NaCl due to having reached the limiting current density (limited by internal resistance 60–80 Ω). The reason for the increased performance of the CapMix process combined with the BES could only have been due to the ionic currents. Further background regarding the ionic currents or fluxes is provided in the ESI.†

Evaluating the effect of BES current on CapMix energy extraction

The energy extracted by CDP charging was calculated from the area inside the voltage versus charge accumulation curve over each cycle (Fig. 4). Energy recovery with BES operation was 59 ± 10 mJ g⁻¹ cycle⁻¹ (2 mA) or 175 ± 16 mJ g⁻¹ cycle⁻¹ (4 mA), compared to only 2.7 ± 0.1 mJ g⁻¹ cycle⁻¹ for controls (no ionic current) (Fig. 4). The energy which can be extracted from the capacitive electrodes in the presence of an BES with a constant discharge of 2 mA is equivalent to nearly 19 cycles from the CDP process without an BES. When the BES was operated at 4 mA the energy extracted in one cycle was comparable to nearly 60 cycles without the BES. In addition to this energy extracted by the capacitive electrodes, ~200–300 mJ cycle⁻¹ was extracted from organic matter using the BES over its complete cycle.

Effect of CapMix on microbial fuel cell performance

The operation of the three-chamber BES allowed for greater peak power densities than achievable in a single chamber BES (Fig. 2s†), however, the voltage and power fluctuated during the CDP four step process (Fig. 5a & b). In particular, the performance decreased during Steps 2 and 3 due to the addition of a large resistance (low concentrate chamber). The BES’s operational power at 4 mA decreased from 1.41 ± 0.03 W m⁻² (cathode) to 0.44 ± 0.09 W m⁻² (cathode) when the high concentrate was replaced by the low concentration (NaCl). When the BES was operated at 2 mA, the BES power decreased...
from 1.03 ± 0.01 W m⁻² (cathode) to 0.71 ± 0.05 W m⁻² (cathode) (Fig. 5b). The intermittent addition of the low concentration solution was therefore detrimental to the BES operation, but necessary for CapMix power production. One way to reduce this resistance would be to design the system to have a thinner CapMix chamber.

**Capacitive mixing with thermolytic salts**

The performance of the CapMix electrodes was further examined using AmB high and low concentration solutions in the middle CapMix chamber, and a high concentration of AmB in the cathode chamber. The switch to AmB as the electrolyte did not significantly alter the capacitance of the electrodes compared to NaCl, with ~80–90 F g⁻¹ obtained for both electrolytes based on cyclic voltammetry tests (5 mV s⁻¹ scan rate) (Fig. 1s†). The use of AmB reduced cathodic resistance, increasing the systems limiting current (5 mA). At this higher current, the energy captured increased to 314 ± 21 mJ g⁻¹ cycle⁻¹ (Fig. 6), which was ~6× more than that previously obtained using CDP. The increased limiting current with AmB compared to NaCl was due to the reduced overpotential of the cathode (Fig. 2s†) because ammonium functions as a proton shuttle, which improves oxygen reduction. The cathode potential was therefore ~200 mV higher at current densities in AmB than in NaCl.

Power densities for the CapMix electrodes with CDP charging using AmB reached 942 ± 175 mJ g⁻¹ cycle⁻¹ (average 301 ± 40 mJ g⁻¹ cycle⁻¹), which approached levels previously obtained using only PRO, RED, or forced CDP processes. AmB increased the overall energy extracted through the CDP process relative to NaCl solutions. At a current of 4 mA, 244 ± 30 mJ g⁻¹ cycle⁻¹ was extracted using AmB, compared to 175 ± 16 mJ g⁻¹ cycle⁻¹ using NaCl. The advantage of the CapMix process compared to RED is that this power is extracted using only a pair of membranes, although the four-step charging cycle is more complex than that needed for RED operation. The advantage of CapMix compared to PRO may be that membrane fouling is reduced as water does not need to flow through the membrane as it does in PRO.

**Forced charged CapMix using the BES**

Power generation and energy extraction using the CapMix process was further examined using the BES to directly charge the CDP electrodes in AmB. This forced charge method avoided the need for an external power source, as the power was provided directly by the BES. To force charge the CapMix electrodes, the BES anode was connected by a wire to the anion-coated capacitive electrode, and the cathode was connected to the cation-coated capacitive electrode. Forced charging increased the potential of the capacitive electrodes to ~0.65 V after five minutes, which allowed increased energy extraction from the capacitive discharge process. The peak voltage increased from ~0.1 V to ~0.85 V (Fig. 7a), and peak power densities increased 8.5× to 7.6 ± 0.1 W m⁻² (0.67 ± 0.08 W m⁻², averaged over the discharge curve) compared to non-forced conditions (Fig. 7b). The energy extracted from the CapMix process increased 47× to 14 900 ± 400 mJ g⁻¹ cycle⁻¹.

Power densities were further increased to 20 W m⁻² (capacitive electrode) when the discharge external load was reduced. However, at this lower external load the high rate of discharge caused an increase in leakage current, which reduced the net energy recovered (Fig. 7s†). The charge obtained through the discharge was due solely to initially invested charge from the BES, and not from the CapMix process. When the charged capacitive electrodes were exposed to the low concentration, the voltage increased from 0.5 V to nearly 0.75 V. However, when connected to an external load, the voltage of the capacitive electrodes immediately decreased to a voltage below that of the

---

**Fig. 6** Total energy extracted with the BES set at different fixed currents using high (500 mM) and low (10 mM) concentration solutions of ammonium bicarbonate (AmB) or sodium chloride (NaCl) in the CapMix chamber. Energy extracted was normalized per gram of capacitive electrode.

**Fig. 7** Performance of the capacitive electrodes with forced charging using the BES: (a) capacitive electrode voltage; and (b) power densities (normalized to a single capacitive electrode area).
initial charge (0.5 V). Further optimization of materials and membranes to reduce charge leakage could therefore improve power densities using this approach.

Conclusions

Capacitive and battery-type electrode approaches offer novel methods for producing electrical power using naturally-occurring (seawater/river water) or engineered (thermolytic solution) salinity gradients. The use of an ionically driven current represents a new approach in the development of these technologies as it substantially increased power densities from ~10 mW m⁻² to ~500 mW m⁻² with NaCl, and ~900 mW m⁻² using thermolytic salts. The direct use of the BES electrodes to force charge and energy recovery at either coastal or industrial sites. Water treatment and provide a new method of power generation as it substantially increased power densities using this approach.

Acknowledgements

This research was supported by the National Science Foundation Graduate Research Fellowship Program (Grant No. DGE1255832 to M.C.H.), and a grant from the King Abdullah University of Science and Technology (KAUST) (Award KUS-I1-003-13). We would like to acknowledge Guang Chen for synthesizing the AEM coating and Kelsey B. Hatzell for constructing and characterizing the capacitive electrodes.

References