

Using Flow Electrodes in Multiple Reactors in Series for Continuous Energy Generation from Capacitive Mixing

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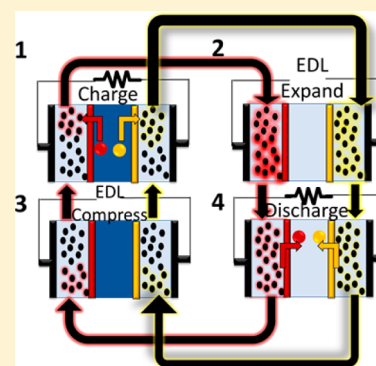
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S Supporting Information

ABSTRACT: Efficient conversion of “mixing energy” to electricity through capacitive mixing (CapMix) has been limited by low energy recoveries, low power densities, and noncontinuous energy production resulting from intermittent charging and discharging cycles. We show here that a CapMix system based on a four-reactor process with flow electrodes can generate constant and continuous energy, providing a more flexible platform for harvesting mixing energy. The power densities were dependent on the flow-electrode carbon loading, with $5.8 \pm 0.2 \text{ mW m}^{-2}$ continuously produced in the charging reactor and $3.3 \pm 0.4 \text{ mW m}^{-2}$ produced in the discharging reactor ($9.2 \pm 0.6 \text{ mW m}^{-2}$ for the whole system). When the flow-electrode carbon loading was 15%. Additionally, when the flow-electrode electrolyte ion concentration increased from 10 to 20 g L^{-1} , the total power density of the whole system (charging and discharging) increased to $50.9 \pm 2.5 \text{ mW m}^{-2}$.



INTRODUCTION

Capacitive mixing (CapMix) is a technology being developed to capture a portion of the $\sim 2.6 \text{ TW}$ of energy that is released by sea and river water mixing at global estuaries.^{1–4} The CapMix energy extraction process is, in theory, the reverse of the emerging brackish water desalination technique termed capacitive deionization (CDI).⁵ One major limitation with both CDI and CapMix is that the desalting (energy consumption) or mixing (energy generation) processes occur intermittently.⁶ This intermittency occurs because the mixing and desalting take place through sequential ion electrosorption and electrodesorption. These two processes typically occur within the same reactor with fixed (solid) electrodes (Figure S1 of the Supporting Information). This operational procedure presents significant challenges for recovering energy from CapMix because inadvertent mixing occurs when the high-concentration (HC) salt solution replaces the low-concentration (LC) salt solution. Another operational limitation is that the power produced varies over the discharge (Figure S1 of the Supporting Information).

The use of flow electrodes, which consist of a suspension of many small capacitive particles in the electrolyte, has provided a means to produce a continuous process for deionization in CDI, energy recovery in flow capacitor systems, and energy production using CapMix.^{7–12} Particles used for flow electrodes are typically large-surface area materials like activated carbon that are added at a high concentration to form a thick slurry in the electrolyte. The specific flow-electrode materials and

electrolytes are chosen on the basis of the desired application. Sodium chloride is the preferred electrolyte for CDI flow electrodes, and acidic electrolytes are useful for energy storage applications.¹³ The active material loading has varied in these different applications, with the limit of the carbon weight percent being $\sim 25\%$, to ensure that the electrode remains flowable. Most studies, however, have limited their carbon loading to 5–15% for CDI applications.^{7,10}

Flow electrodes were previously proposed to create a continuous process from CDI and CapMix using a two-reactor or one-reactor configuration.^{9,11} The two-reactor CDI configuration allowed for continuous desalination in the first reactor and energy recovery in the second reactor. A two-reactor configuration was proposed, but a one-reactor configuration was used for the CapMix study. Within the one chamber, the two flow-electrode electrolytes consisted of seawater and the middle chamber was river water. With this configuration, the flow electrodes could not be recycled during energy generation, as the electrode electrolyte concentration would have eventually equilibrated to that of the middle chamber. Here we show that energy generation with the CapMix process can occur continuously and efficiently when using four separate reactors, with two separate flow-electrode slurries (F-CapMix)

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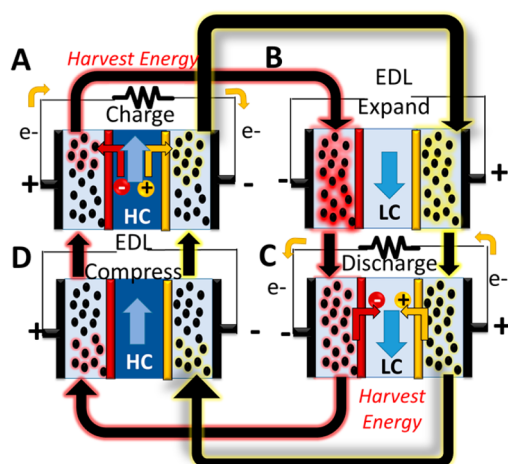


Figure 1. Flow-electrode capacitive mixing based on an energy extraction process using four separate reactors. Flow electrodes (black semispherical particles) are (A) spontaneously charged in reactor 1 using the salty HC solution in the middle chamber, so that energy is harvested, and then transported to (B) reactor 2 where a reverse Donnan potential is established using the less salty LC solution in the middle chamber under open circuit conditions. (C) The flow electrodes enter reactor 3 where energy is again harvested with LC water in the middle chamber, and then (D) the flow electrodes enter into reactor 4 where a reverse Donnan potential is again established under open circuit conditions using the HC in the middle chamber. Note that the voltage in each reactor is constant over time and that electrical power is recovered in both reactors A and C under these conditions (nonforced charging).

(Figure 1). In this four-reactor process, because of the continuous electrode regeneration, a finite volume of flow electrode can be recycled through the reactors. The proposed configuration isolates ion electrosorption, electrodesorption, and electric double-layer (EDL) expansion and compression processes. A two-reactor process may be possible (electrosorption and electrodesorption) for CapMix testing that relies only on the Donnan potential. However, for the force-charging CapMix approach, a significant EDL expansion and compression process occurs postcharging and discharging that can take up to 50 s.¹⁴ Without force charging, this equilibration is shorter but still ranges between 3 and 30 s depending on the electrode geometry.¹⁵ Capacitive mixing without membranes also has an equilibration time that is dependent on the spontaneous potential of the chosen carbon material.⁶ Thus, to capture these transients, the two open circuit reactors are necessary.

In the F-CapMix process, the electrodes are charged in the first reactor by the transfer of ions from the HC solution into the flow electrode through an ion exchange membrane. The flux into the electrodes can take place spontaneously with only the membrane potential (spontaneous charging), providing the first source of continuous and harvestable electrical power. Alternatively, additional charge can be added to the system in the first reactor using an external power source to increase the voltage window (forced charge), but no electrical power can be harvested under these conditions.^{14,16} In the second reactor, the flow electrodes equilibrate to the membrane potential established with an LC solution flowing in the center chamber of the reactor. In the third reactor, energy is harvested through an external load. In the fourth reactor, the flow electrodes equilibrate to the HC solution under open circuit conditions.

By using four reactors in the F-CapMix process, the HC and LC solutions no longer directly make contact between steps. The separation of the four steps allows continuous power generation, and this new architecture may also provide a more effective platform for evaluating new energy extraction materials and processes.^{17,18}

MATERIALS AND METHODS

Reactor Materials. Cube-shaped reactors were constructed using rigid plates of high-density polyethylene (HDPE) (Figure S1 of the Supporting Information). Plastic tube fittings (inner diameter of 0.32 cm) were connected to the end plates to allow flow among the HC, LC, and flow-electrode chambers of the four different reactors, connected using silicone tubing (Masterflex L/S 16, Cole Parmer, Vernon Hills, IL). Current collectors were cut from graphite plates (www.graphitstore.com), with a straight flow path of 3 cm × 0.53 cm × 0.2 cm (length × width × height) cut in the middle of the plate. Ion exchange membranes (Selemion CMV and AMV, Asahi Glass, Japan), each with a projected area of 1.6 cm², were placed on either end of the middle gasket. The power obtained from the charge and discharge chambers was normalized by the membrane area to which one flow electrode was exposed, as is common with previous CapMix reports (6.36 cm²).³ The whole system power is reported as the total power of both the charge and discharge chambers.

Flow electrodes (volume of 20 mL) were prepared at 5, 10, and 15 wt % using activated carbon (YP50 F, Kuraray Chemical Co., Osaka, Japan). The carbon utilized contained mostly micropores with a BET surface area of ~1400 m²/g. The HC and LC solutions (20 mL each) were housed in separate reservoirs. All flow-electrode and feed solutions were pumped at a rate of 5 mL min⁻¹. The HC solution was 30 g L⁻¹ NaCl, and the LC solution was 2 g L⁻¹ NaCl. Conductivities of the LC solution were measured during tests using a conductivity meter (Thermo Scientific Orion VERSA STAR) and probe (Fisher Scientific, Waltham, MA). The charge and discharge chambers were maintained under a constant load (100 Ω resistance) during energy extraction tests.

Energy Calculations. The mixing energy efficiency (η_{mix}) is a measure of the electrical energy extracted through the external load during the discharge phase compared to the amount of energy released through the salt mixing process (entropy change). The system mixing energy efficiency was calculated as

$$\eta_{\text{mix}} = \frac{E_C + E_D}{G_{\text{mix},0} - G_{\text{mix},f}} \times 100 \quad (1)$$

where E_C and E_D are the energies (joules) produced from the CDP process (reactors 1 and 3) and $G_{\text{mix},0}$ and $G_{\text{mix},f}$ are the energies released because of mixing. In this work, all testing was conducted without the addition of additional charge, so the electrical energy could be obtained from both the charge and discharge reactors. The Gibbs free energy of each solution (inlet and outlet) was estimated using solution activities obtained with OLI software (Ceder Knolls, NJ).

The electrical energy efficiency (η_E), calculated as

$$\eta_E = \frac{E_D}{E_C} \times 100 \quad (2)$$

is a measure of the ratio of the actual charge that was stored within the electrode (ion adsorption) in reactor 1 to the charge that is released from the electrodes (ion desorption) in reactor

3. The value becomes increasingly important when additional charge is added to the system.

Reactor Operation. Energy generation with the flow-electrode-based CapMix method occurred in four separate reactors (Figure 1A–D). Each reactor contained three flow channels formed using one anion exchange membrane (AEM) and one cation exchange membrane (CEM) (Figure S2 of the Supporting Information). Two channels on opposing sides of the center chamber contained the flow electrodes, consisting of carbon particles in a sodium chloride electrolyte. The middle chamber held the salt solution (either HC or LC).⁷ In reactor 1 (Figure 1A), the electrodes were charged under a constant load (resistor) while the HC flowed through the middle chamber. The potential used to drive counterions into each electrode (positive and negative) is dictated solely by the Donnan potential that forms at each membrane (AEM and CEM) interface ($U_{\text{cell}} = U_{\text{AEM}} + U_{\text{CEM}}$), and therefore, this potential is spontaneous. Once charged, the flow electrodes flowed into the second reactor, where in open circuit the membrane polarity was reversed because of the presence of a LC solution in the middle chamber (Figure 1B). The charged electrodes flowed to the third chamber where the electrodes were discharged (ions desorbed) under a constant load (resistor). This reactor accomplished energy harvesting through the mixing process (Figure 1C). Once discharged, the electrodes were sent into a fourth reactor where the membrane potentials were reversed again under open circuit conditions, by changing the middle chamber solution to a HC solution (Figure 1D).

The electrodes can be continuously recycled through each chamber in series through the four reactors, while the salt solutions (LC and HC) are similarly recycled in a closed loop through their respective middle chambers. Thus, the flow-electrode, LC, and HC solutions and do not directly interact. As a result, each reactor maintains a constant potential/current over time.

RESULTS AND DISCUSSION

Flow-Electrode Carbon Loading. The four-reactor continuous flow process was initially examined using a constant electrolyte ion concentration of 10 g L^{-1} , with the mass loading of the activated carbon flow electrodes varying from 0 to 15 wt %. The increased carbon loading produced steady state charge voltages (after 10 min) in reactor 1 of $2.0 \pm 0.7 \text{ mV}$ (5 wt %), $8.8 \pm 0.8 \text{ mV}$ (10 wt %), and $14 \pm 2 \text{ mV}$ (15 wt %) (Figure 2A). The maximal charge power density with 15 wt % approached $5.8 \pm 0.3 \text{ mW m}^{-2}$ (Figure 2B). The steady state discharge voltages in reactor 3 similarly increased with carbon loading from $-1.7 \pm 0.4 \text{ mV}$ (5 wt %) to $-9.6 \pm 0.9 \text{ mV}$ (10 wt %) and $-19 \pm 1 \text{ mV}$ (15 wt %) and resulted in a maximal discharge power density of $3.3 \pm 0.4 \text{ mW m}^{-2}$. The total constant power produced from the system approached $9.2 \pm 0.6 \text{ mW m}^{-2}$.

The potentials observed with 15 wt % flow electrodes approached the midpoint of the discharge voltages reported in testing conducted with solid film electrodes (approximately ± 15 – 20 mV). Steady state open circuit voltages established with the middle chamber housing the HC and LC solutions (reactors 2 and 4) were equal to (HC) or greater than (LC) the peak voltages obtained with film electrodes (Figure S3 of the Supporting Information).³ The higher voltage observed with the LC (reactor 2) is due to the Donnan potential established with the flow electrode being larger than the potential that could be established with a film electrode. Here the flow-

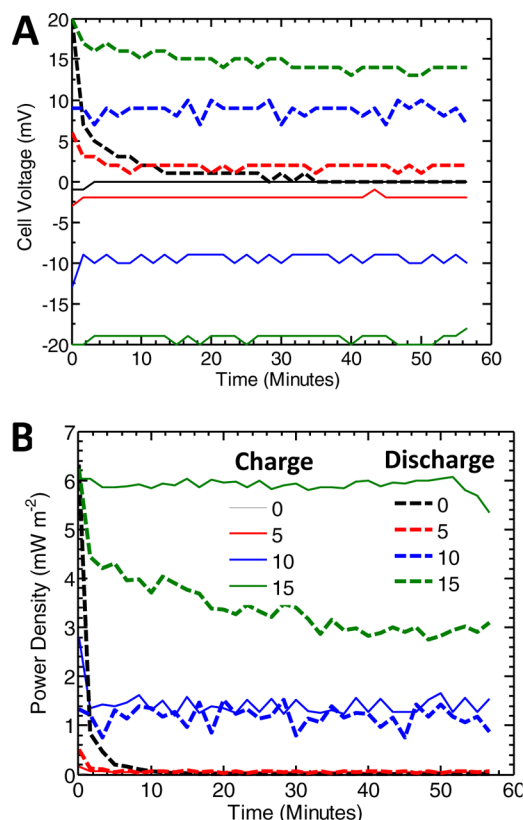


Figure 2. (A) Constant voltages and (B) power densities during spontaneous charging (reactor 1) and discharging (reactor 3), with carbon loadings of 0, 5, 10, and 15 wt %. The flow-electrode electrolyte concentration was fixed at 10 g L^{-1} , and the power density was normalized by the total anion exchange membrane area in four reactors.

electrode ion concentration was 10 g L^{-1} , whereas the ion concentration in the film electrode was solely dependent on the electromigration of salt into the pores. The higher power density produced during the charge phase was attributed to the reduction in whole cell resistance with the HC solution in the middle chamber. These power densities were slightly lower than the midpoint power densities previously obtained with solid film electrodes ($\sim 20 \text{ mW m}^{-2}$), but here the power densities were nearly constant and continuous. High power densities may be able to be achieved through decreasing the cell resistance, and through varying the external load. No voltage [$(\sim 0.05 \pm 2) \times 10^{-4} \text{ mV}$] was produced in the absence of the flow electrodes.

Flow-Electrode Electrolyte Ion Concentration. The whole cell potential is due to the membrane potentials produced under the different operational conditions. With solid film electrodes, this Donnan potential is directly related to the activity of the ions in the carbon pore, and the activity of ions in the bulk solution. With a flow-electrode system, the membrane potential is generated on the basis of the electrolyte ion concentration in the flow electrode and the bulk solution concentration. Thus, the membrane potential in a flow-electrode system is primarily dictated by the electrolyte concentration. When the electrolyte ion concentration was increased from $\sim 0 \text{ g L}^{-1}$ (deionized water) to 20 g L^{-1} , the charge potential in reactor 1 increased from -42 ± 0.5 to $-11 \pm 0.6 \text{ mV}$ and the discharge potential in reactor 3 increased from -4.8 ± 0.7 to $56 \pm 1.2 \text{ mV}$. These changes resulted in an

increase in the power output from $\sim 0.3 \pm 0.1$ to $\sim 49 \pm 2.3$ mW m^{-2} from the discharge reactor (reactor 3) and a decrease in power density from $\sim 28 \pm 0.9$ to 2 ± 0.2 mW m^{-2} in the charge reactor (reactor 1). Ultimately, there will be a trade-off between maintaining high charging and discharging power densities and maximizing the total power produced from the entire system. The maximal whole system power output approached 50.9 ± 2.5 mW m^{-2} (Figure 3).² The power output from reactor 3 with an ion concentration of 20 g L^{-1} was similar to that reported in a previous single-chamber flow CapMix study ($\sim 30 \text{ mW m}^{-2}$).⁹

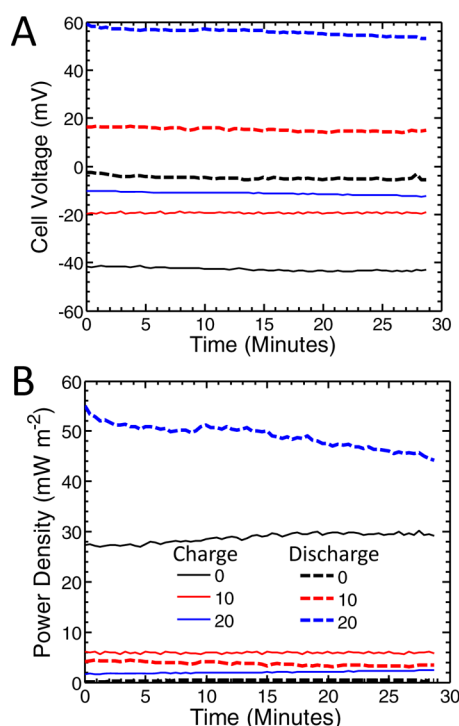


Figure 3. (A) Constant voltages and (B) power densities during spontaneous charging (reactor 1) and discharging (reactor 3), with different flow-electrode electrolyte salt concentrations of ~ 0 (deionized water), 10, and 20 g L^{-1} . The carbon concentration was fixed at 15 wt %, and power densities are normalized by the total anion exchange membrane area in four reactors.

Over a period of time more extended than that examined here, it is expected that the flow-electrode ion concentration would equilibrate to a concentration between seawater and river water (e.g., 15 g L^{-1}). Thus, while some advantages in terms of power output could be obtained through increasing the ion concentration in the flow electrode (e.g., 20 g L^{-1}), this would not be maintained over the entire test. This can be observed by the slight decrease in the discharge power when 20 g L^{-1} was the electrolyte salt concentration (Figure 3).

Electrical Energy Efficiency and Mixing Energy Efficiency. Through complete separation of the HC and LC flow channels, most of the mixing produced in reactor 3 was due to ion electrodesorption and charge leakage through the membranes. Overall, the change in the salt concentration of the LC chamber was minimal ($\leq 0.8\%$) over the test period (Figure S4 of the Supporting Information). With the high weight percent loading, the energy harvested (E_D) was 2.7 mJ with 10 wt % flow electrodes and 7.7 mJ with 15 wt % flow electrodes. The energy harvested in the charge phase was 5.6 and 11.5 mJ

for 10 and 15 wt %, respectively. This produced electrical energy efficiencies of $\sim 48\%$ (10 wt %) and 67% (15 wt %).

The mixing energy efficiencies were only $\sim 1.3\%$ (10 wt %) and 2.3% (15 wt %). While these appear to be low, they are reasonable given the small voltage window produced solely by the ion exchange membranes. Assuming a voltage window of ~ 50 – 100 mV and a standard capacitance of the carbon material (50 – 100 F g^{-1}), the achieved 1–2% efficiency approaches that expected from theory (~ 10 – 30 mJ) (Figure S5 of the Supporting Information).

Energy generation from CapMix is dependent on the energy input (charge stored), and therefore, forced charging must be used to increase the voltage window and improve overall energy production.^{14,16} While forced charging requires electrical power input in reactor 1, the larger voltage window produced in reactor 2 would be expected to allow increased energy recovery, as previously shown for fixed electrode systems.¹⁴ Therefore, forced charging and further development should allow improved power production.³ Further increases in carbon loading and reducing electrical losses through improved reactor designs may also increase the overall system efficiencies.

■ ASSOCIATED CONTENT

Supporting Information

Reactor design, electrochemical testing, and additional basic modeling is provided in the supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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