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An Entrochemical Water Heater

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AN ENTROCHEMICAL WATER HEATER

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ABSTRACT
Entrochemical systems are systems capable of generating internal thermal gradients through internal water movements which simultaneously transfer get of vaporization between internal water reservoirs. These systems move to a chemical equilibrium state that generates and maintains a thermal gradient. Entrochemical thermal batteries (ETB) can be constructed which extend the thermal gradient of a single cell through an additive process. Such systems can deliver useful work. Additionally solutions used therein may be recharged passively using environmental heat.

We describe the design and function of a bench-scale water heater capable of heating a small water reservoir. The system is powered by an ETB. We characterize its function utilizing ETBs of one and three cells. We calculate peak wattage of 99.17 W for a single cell system and peak wattage of 72.39 W across a three-cell array. The limited change in wattage across an array compared to a single cell indicates that the overall wattage is dominated by a single-cell performance rather than dynamics introduced by the array.

KEYWORDS: entrochemical system, environmental heat, water heating

INTRODUCTION
Recently, our laboratory has done significant work on a class of devices known as entrochemical devices. These are devices that generate internal thermal gradients using a spontaneous entropy transfer between a solvent pool and a desiccant solution pool made with the same solvent. This work has demonstrated how to construct entrochemical thermal batteries (ETB), devices that are capable of generating significant internal thermal gradient (Luo et al., 2015) using a spontaneous process known as the entrochemical process. Like absorption refrigeration (Srikhirin et al., 2001), the process involves the spontaneous movement of water from one water pool to a second water pool containing a higher concentration of dissolved substances than the first. The movement of water, mediated by evaporation and condensation, transfers the heat of vaporization between water bodies. Entrochemical thermal batteries are made up of a plurality of connected entrochemical cells. By thermally coupling the cold part of one cell and the warm part of the adjacent cell, the overall thermal gradient can be amplified beyond what a single cell can produce (Kazadi et al., 2015).

The use of entrochemical devices as an enabling technology for water heaters provides a number of advantages. The thermal energy utilized in a water heater can be acquired from environmental thermal energy. This is enabled through the development and maintenance of a thermal gradient. The cold end of the device can be colder than ambient, enabling heat to be absorbed spontaneously. The warm end can then deliver this absorbed heat at an "amplified" temperature that is significantly higher than ambient.

Perhaps the most important aspect of entrochemical systems is that the desiccant solution can be reconcentrated through a process of simple evaporation. As a practical matter, evaporation can be enhanced by using airflow, which can be delivered using solar chimneys (Schlaich, 2002), passive wind-generating devices capable of transforming solar insulation into airflow. Theoretically, such a device could enable the evaporative process to exceed the energetic potential of direct insulation (Kazadi et al., 2013). The airflow enables evaporation of the water absorbed during the heat-transferring stage of the entrochemical system. The evaporative process transfers entropy from the liquid to the air and amplifies it. It is therefore spontaneous. Moreover, the thermal energy which drives the process comes from the air. Thus, the energy required to drive the system literally comes from the air. Work on the design and efficacy of solar chimneys continues (Kazadi et al., 2015).

Additionally, the system can be designed to store recharged desiccant solution, irrespective of the source of the energy for recharge. This stored desiccant can be viewed as stored energetic potential, capable of driving the subsequent heating of the water tank. The volume of desiccant required to enable the requisite heating is
significantly smaller than the tank size of conventional thermal storage tanks for solar water heaters. As an example, storage of 30 kWh in a conventional tank 40°C above ambient would require a tank of 170.9 gallons (Ryan et al., 2010). The same energy stored in an entrochemical storage system would require 38.3 gallons. The stored energetic potential is stable and does not leak off in time. Unlike electrical storage (Liu et al., 2012) or thermal storage, the storage of chemically inert salt solutions does not change, as long as it is stored in non-corroding tanks. This means that storage can be built up over long periods of time and that unused energy can be saved for later use. This is particularly important for households during the times of day when energy is available from sunlight or wind.

**DESIGN OF AN ENTROCHEMICAL WATER HEATER**

An entrochemical water heater (EWH) is a water heater in which the heat entering the water is absorbed from the environment at the cold end of an entrochemical thermal battery and is subsequently amplified before being injected into the water. The device is depicted pictorially in Figure 2.1.

![Figure 2.1: A conceptual depiction of an entrochemical water heater and a photo of our experimental apparatus.](image)

In this Figure, the ETB supplied heat to the water heater (left) at the warm end of the ETB. The cold side (right) of the ETB is exposed to the external environment where it can absorb thermal energy. The absorbed thermal energy is amplified and delivered to the end. We designed a water heater based on the ETB system. We utilize a three-cell ETB comprising four adjacent acrylic chambers, numbered 1 through 4, and two steel chambers embedded within chambers 2 and 3, numbered 5 and 6. Chambers 1, 5, and 6, contain water, generally obtained from the laboratory tap. Chambers 2, 3, and 4 contain saturated CaCl₂ (Lowenstein et al., 2006) solutions. Chambers 1 and 2 are connected via a vapor pathway, as are Chambers 5 and 2, and chambers 6 and 3. The vapor pathways end in the chambers containing CaCl₂ solutions with a bubbling tube. The bubbling tube injects water vapor from the connecting water chamber below the surface of the CaCl₂ solution. As chambers 5 and 6 are embedded within chambers 2 and 3, the temperatures of the liquid in chambers 2 and 5 are less than 0.1 °C apart, as are the temperatures of chambers 3 and 6. An additional steel chamber containing a maximum of 110mL is embedded within chamber 6, and this forms our heated water reservoir. Chamber 1 can be enhanced with a steel chamber embedded in its bottom, enabling heat to come into the chamber from the surrounding room.

As indicated above, each entrochemical cell is independently capable of generating a thermal gradient. The cells comprise the connected water and solution reservoirs. Together, the system can generate a sizable thermal gradient, enabling the water within the water tank to be heated. Heat is transferred from chamber 1 to chamber 4 and into the water tank via the combination of cells.

**PERFORMANCE**

We measured the performance of the heating function of the water heaters by placing a thermistor (Omega Part #: HSTH-44034-80) in the water tank. We measured the heating phase of the tank after the ETB was activated by generating wet vacuums in each of the cells. Typical runs from this heating phase are given below in Figure 3.1.
Figure 3.1: Heating phase of the entrochemical water heater in a room at 25°C.

Figure 3.1 (A) illustrates three typical runs in a single cell water heater. In all three runs, the temperature gradient rapidly increases from zero to approximately nineteen degrees Celsius. The system stabilizes at this temperature, slowly losing the thermal gradient over time. While there is some variation in the speed with which the system achieves this temperature, it produces similar performance upon stabilization.

One time trace exhibits a significant jump at twelve minutes. An increase in temperature of 2.00°C occurs rapidly over a period of two minutes. This is a significant jump, and it occurred at a point when the vacuum pump was run an additional time. The system, at that point, stabilizes to a higher temperature and begins a slow decline. It is hypothesized that air remaining in the less saline water after the first vacuum purge is moved to the salt chamber along with water vapor. This would tend to raise the air pressure in the more saline chamber, reducing the airflow and therefore wattage from the salt chamber. It would also contribute to a slow decline in system performance. Running the vacuum a second time tends to remove some of this air, therefore restoring and augmenting the overall system performance.

Similarly, the typical temperature differences in the three chamber system (Figure 3.1 (B)) produce consistent performance, with the same anomalous behavior of a single trace. This trace corresponds to a system which was initially vacuum-purged for nearly a minute, while the remaining two were purged for half that time. As a result, the system takes a bit longer to get going initially, but rapidly overtakes the other two runs, establishing a higher thermal gradient.

The enhancement of using the thermal battery is readily apparent. The single cell system stabilizes at 19.2−21.5°C while the three cell system stabilizes at a temperature gradient of 31.99−35.75°C.

From these data we are able to determine the wattage of the heater. Using the weight of the water and type 304 steel, we can back calculate the wattage. Note that these are net wattage and include the deleterious effects of thermal leakage in the device. These data are given below.
The heating power of both a one- and a three-cell-system are graphed in Figure 3.2. The wattage is maximal at minimal thermal gradient. It is at this point that the movement of water, driven by differences in vapor pressure, is maximal. Interestingly, the maximal wattage seems to be similar for both single and three cell systems. The wattage for a single cell is measured at a maximum of 99.17 W at nearly zero degrees' thermal gradient while that for three cells is measured at a maximum of 72.39 W at nearly 8.827°C thermal gradient across the array. The graphs for the multiple chamber system appear to be shifted to the right in comparison to the single chamber graphs.

ENERGY CYCLE AND ENERGY STORAGE
The entrochemical water heater has two operational cycles which define whether it is part of a system consuming energy or part of a system harvesting energy. The closed energetic cycle results from entrochemical water heaters that are physically closed and so retain all of their water and salt. Open energetic cycles result from entrochemical water heaters that are physically open or quasi-open and so receive and emit water.

Closed energetic cycle
The closed energetic cycle is depicted below in Figure 4.1.

In step one, the water heater functions via the movement of heat from the surrounding room into the water tank. As one portion of the device is relatively cool, it tends to absorb heat from the surroundings. When this energy is transferred to the progressively warmer chambers and then on to the water tank, some portion of it is consumed as entropy increases. The remaining energy is delivered to the water tank.

The next part of the cycle involves the drying of the dilute draw solution. This is achieved by using thermal or mechanical methods to remove water from the solution. Examples include vacuum distillation, reverse osmosis, or thermal distillation. The water that is removed is recovered and cycled back into the system. This is the
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closed configuration. This configuration generates clean water in the drying stage and generates an additional quantity of water in the next cycle, effectively increasing the output given any energetic input. This configuration is depicted in Figure 4.1.

Given an energetic input of $\Delta U_{in}$ joules, the drying process produces a quantity of water given by $f_w(\Delta U_{in})$ and a quantity of concentrated solution given by $f_s(\Delta U_{in})$. When recombining this amount of water and solution, the amount of energy delivered is equal to

$$\Delta U_{net} = \Delta V_I H_V + \sum_{i=1}^{N_{eff}} \left( T_i \Delta V_i \ln(x_i) + T_i (V_i - \Delta V_i) \ln \left( \frac{x_i}{x'_i} \right) \right) \tag{1}$$

where

$$\Delta V_{i+1} = \Delta V_i + \frac{1}{N_e} (T_i \Delta V_i \ln(x_i)) \tag{2}$$

and $x_i$ represents the ratio of water to solution. If $\Delta U_{net} \leq \Delta U_{in}$, the process is a net user of energy, however, $\Delta U_{net} > \Delta U_{in}$ then the process is a net producer of energy. As an example, the theoretical minimal energy for reverse osmosis at 6.12 molar salt water is 8.47 kWh/m$^3$ usage per stage (or no entropic losses) and three stages, the energy output is 627.7 kWh, more than 74 times the input. This not only absorbs and stores energy, but amplifies it as well.

**Open energetic cycle**

A second, open energetic cycle for the distiller is depicted in Figure 4.2.

![Figure 4.1: The open energetic cycle for the water heater](image)

In the open energetic cycle, the solution is dried through evaporation. As the draw solution is an aqueous solution of relatively low chemical activity, it can be dried by direct exposure to air with a temperature equally greater than room temperature. In this scenario, the energy required to achieve the recharge is the heat of air, making it a direct energy source driving the distiller. While this does not recapture the water that enables the internal heat transport, it does eliminate the need for an additional energy source outside of that required to generate the initial wet vacuum and operating valves.
Energy storage
An extremely attractive feature of the entrochemical water heater is the ability to create and store matter in a low entropic state. This generates energetic potential, or the ability to utilize an entropy transfer to acquire environmental thermal energy. The storage of the energetic potential is enabled by stage of the concentrated desiccant solution. The solution can be stored virtually indefinitely with negligible change to its chemical state. This eliminates a common problem with solar thermal systems whose energy storage is limited to storing hot water in the tank that will be used.

DISCUSSION
This study centers on a bench scale water heater with a tank size of approximately 110 mL. Our goal is to be able to repeatedly heat the water in the tank relatively quickly. We seek a system design that enables us to accomplish this using an ETB. The current system incorporated a small tank in the ETB and was able to function repeatedly with similar performance data each time.

One of the goals of the study is to develop a benchmark for system performance. We determined that the lower bound on wattage of a single cell with an ambient temperature of 25 °C is 100 W. We then measured the same on a linear battery design incorporating the EBT. This system nearly matches the performance of the single cell at 73.39 W. This wattage happens at a higher thermal gradient than that of the single track that of the single cell well, albeit shifted to higher thermal gradients. As a result, it appears that the system’s performance is much more heavily influenced by the capabilities of the single cell than the array. The differences in performance may be strongly related to thermal leakage; no insulation was used in the system and the warmth / coolness is readily felt on the exterior of the device. Much of the heat may be leaking out of the system rather than being transferred to the tank.

The size of the device compared to its wage is a limitation of the current design. Scaling up to a ten gallon tank would require wattage of at least 2.1 kW in order to heat the water (and not the tank) within 30 minutes. This would require at least 21 parallel arrays of the current design and the size would be prohibitive. As a result, it is important to begin the work go miniaturization. Current limitations exist as a result of the need for water vapor to pass through corridors that can be effectively sealed by water droplets due to their high surface tension. Improving these corridors might enable miniaturization and increasing energy densities.

CONCLUSION
Work on entrochemical systems is aimed at generating systems that can carry out tasks requiring energy in which a large amount of the energy being utilized is environmental. Water heating is a task that is undertaken by virtually every society on earth and uses an enormous amount of energy. It is the second largest domestic water use and, as such, is both a great cost and a huge source of greenhouse gas emissions.

In this paper we have described the design and characterization of the use of an entrochemical water heater. The water heater generates a thermal gradient of as much as 35.75°C and uses this to heat a small tank of water. The cold side of the battery reaches temperatures of 11 − 13°C, significantly colder than the room’s 21 − 23°C. As a result, heat enters the cold side through a stainless steel tank, providing environmental heat for the water tank. Effectively, the water tank is warmed using environmental heat.

Providing the concentrated solution that drives this process is possible via two general strategies. In one, work can be done to reconcentrate the solution. This requires generated energy, but many physical processes can use significantly less energy to reconcentrate the solution than the energy that the forward reaction makes available. As a result, the system can be set up as a type of “breeder reactor”. In the second strategy, evaporative processes remove water from the dilute solution, restoring its concentration. New replacement water is used to regenerate the internal water reservoir. No generated energy is used for either process and the system is a source of thermal energy.

We measured the heating capacity and wattage of a three cell system alongside that of a single cell system. Both showed similar maximal wattages though the three cell system exhibited nearly twice the heating capacity of the single cell system. The wattage was not limited by nor enhanced by the batter structure. As a result, the thermal transfer within a cell is likely to be significantly larger than the movement of heat within a single cell. Increasing the wattage of a system would require more parallel cells as oppose to longer batteries.
This work produced and characterized a bench scale device with a water tank holding only 111 mL. Future work will improve the insulation surrounding the battery and investigate the use of a larger tank and higher wattage parallel arrays.

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NONMENCLATURE

| W   | Wattage, J/s |
| kWh | Kilowatt hour |
| ºC  | Celsius      |
| mL  | Mililiter    |
| kWh/m³ | Kilowatt hour per cubic meter |
| Uₐ | Energetic input, J |
| Hᵥ | Heat of vaporization of water, J/g |
| V₁ | Volume in first chamber, mL |
| Vᵢ | Initial volume, mL |
| Tᵢ | Initial temperature, J |
| xᵢ | Ratio of water to solution |

REFERENCES


