

# Entrochemical thermal battery design for atmospheric heat collectors

S. Kazadi, S. Kim, X. Xu, W. Gong, A. Gupta

May 31, 2015

## Abstract

We present two novel design modifications to the basic entrochemical system which enable the generation of an entrochemical thermal battery. The inclusion of a passive mixing mechanism enables the continual disruption of the water layer that forms at the top of the saline solutions, enhancing the overall thermal gradient. Embedding of one cell's cool side in the previous cell's warm side allows efficient conduction of thermal energy between the two, effectively driving the additive property of the overall thermal gradient, the *battery effect*. We demonstrate that the passive mixing mechanism enhances performance, generating a one-cell gradient of  $18.3 \pm 0.3^\circ\text{C}$  rather than a non-mixed gradient of  $10.3 \pm 1.5^\circ\text{C}$ . Using the battery effect, we are able to obtain a three-cell thermal gradient of  $40.2 \pm 0.3^\circ\text{C}$ . Using the current uninsulated chambers, a projected asymptotic thermal gradient of  $64.71^\circ\text{C}$  is determined for many independent cells.

## 1 Introduction

Interest in renewable energy is currently widespread and growing. Anthropogenic climate change is providing an impetus to look for new sources of renewable energy. A majority of the current work on renewables is centered around photovoltaic and wind systems. Yet renewable energy sources have also been suggested which center around salinity gradient-based methods [10, 5, 7, 8, 9]. These are attractive because the energy is derived from heat and is already in the system; it need not be tied to wind or solar cycles.

Another heat-based energy source is an *atmospheric heat collector*. This is a device that absorbs environmental thermal energy and makes it available to do work. Contrary to the erroneous common belief that this is a process that violates the laws of thermodynamics[4], the fact that our planet is energetically open and experiences a bidirectional daily energy flux makes such a device possible. In one in-

stantiation, it is a device that implements two different processes. Step one in this process uses a spontaneous heat pump to generate an actively maintained thermal gradient in a closed device, mediated by internal water transfers. Heat spontaneously enters the cold side, and the warm side is warm enough to do work. Step two in this process evaporates water from a solution used by the heat pump in Step one, effectively recharging it, by running relatively dry airflow from a solar chimney over the solution. Together, these processes enable environmental energy to be acquired, in particular, as a heating process. The process was first described by Kazadi et. al. in 2013[2].

The heat pump in step one is an entrochemical system in which two solutions of differing salinity spontaneously generate a thermal gradient[3]. In order for the more concentrated and warmer solution to be able to be recharged, it must be filled with a salt solution that is of relatively low osmolarity. Yet using salt solutions of low osmolarity limits the magnitude of the thermal gradient one can obtain in a single device. As a result, in order to generate the large thermal gradients needed, the entrochemical system must be a battery, in which multiple individual systems independently generate thermal gradients and their gradients are summed to form a larger and more useful thermal gradient.

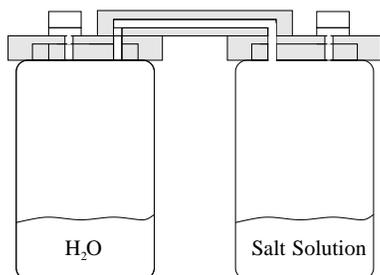
Previous attempts to develop batteries [3] have been limited to only two cells and relatively small thermal gradients of a few degrees Celsius. Such small thermal gradients are virtually useless as drivers of any industrial process. In this paper we present an improved battery design that succeeds in developing significantly higher thermal gradients of several tens of degrees Celsius using  $\text{CaCl}_2$  solutions - solutions that can be dried in a solar chimney. As a result of this design improvement, the combined system is capable of acquiring thermal energy to dry the solution and then using the solution to enable a heat pump that can acquire additional heat energy, making it available to do work.

This paper is organized as follows. Section 2 dis-

cusses the detailed design of a nested thermal battery structure. Section 3 describes experiments conducted to validate the performance of the thermal battery. Section 4 discusses the results of the experiments. Section 5 concludes the paper.

## 2 Eliminating the surface effect

Figure 2.1 is a diagram of the basic entrochemical device which generates a thermal gradient when a wet vacuum<sup>1</sup> is established therein.



**Figure 2.1:** The basic entrochemical device.

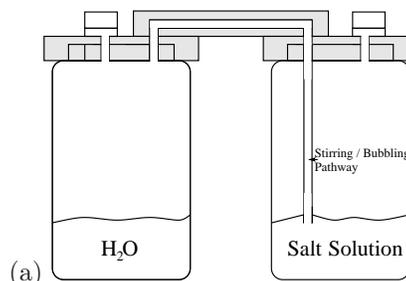
The basic entrochemical device comprises two chambers in vapor communication. Each chamber contains a quantity of water and one of these quantities of water has a significantly greater salinity than the other. In the presence of a wet vacuum and particularly if the chambers are constructed from good thermal insulators, the two water bodies equilibrate at different temperatures. This results from the alteration of the solvent's chemical potential as a result of the addition of salt and the need to reach chemical equilibrium.

Heat is moved, in practice, by water evaporating from the less saline water and condensing on the more saline water. The relatively lowered vapor pressure in the combined vessel is lower than the less saline water's equilibrium vapor pressure and higher than the more saline water's equilibrium vapor pressure. As a result, the less saline water begins boiling while the more saline water begins absorbing water vapor. The condensation of water on the more saline water has the effect of decreasing the surface concentration of the water, effectively reducing the overall effect. When this occurs in combined systems, the effect can lead to internal reversals of thermal gradient due to interactions of adjacent cells.

In order to eliminate the condensed water film, the saline solution is mixed. There are many mixing

<sup>1</sup>A *wet vacuum* is a vacuum in which the air has been pushed out and replaced by the vapor state of the solvent in one or more solutions contained in the chamber under vacuum.

mechanisms available, and initial experiments consisted of manually mixing the solution with a stir-bar or with manual agitation. Any mixing mechanism, however, consumes energy, and it is important to ensure that the energy used does not cannibalize that energy one wishes to extract. As a result, the mixing mechanism settled on, illustrated in Figure 2.2, utilizes the thermal energy being transferred as a method of agitating the solution. The mechanism comprises a partially submerged tube that terminates the vapor passageway from the chamber containing the lower salinity solution to the chamber containing the higher salinity solution. The greater vapor pressure of the chamber containing the lower salinity solution forces vapor through the tube despite the end being submerged in the higher salinity solution. The resulting vapor bubbles serve the dual purpose of efficiently injecting vapor into the higher concentration solution and agitating the solution itself and providing mixing<sup>2</sup>.



**Figure 2.2:** The single cell device with a lowest-energy mixing mechanism installed. (a) is a diagram of the device while (b) is the laboratory model.

<sup>2</sup>It has not been shown that this is the lowest-energy mixing mechanism possible, though we do offer it as a conjecture.

### 3 Nested entrochemical systems

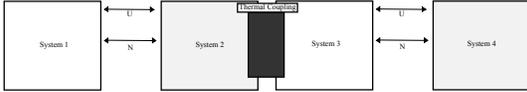
A single pair of chambers comprising an entrochemical system can generate a limited thermal gradient. This thermal gradient may be expanded by choosing an appropriate salt. However, salts that generate very large thermal gradients of greater than  $20^\circ\text{C}$  are so deliquescent at the concentrations required to generate these thermal gradients that their salt solutions tend to dry air flowing over them rather than tending to humidify the air. As a result, work cannot be done on them by environmental airflow; the system cannot be recharged with these salts.

In order to obtain the thermal effect of having high concentration salt solutions in the reaction chamber, we can combine the different entrochemical systems so as to generate *thermal batteries*.

#### 3.1 The Battery Effect

The *battery effect* refers to the additive effect on the overall thermal gradient of thermally connecting two or more different entrochemical cells. The effect may be understood as follows.

Suppose that we create a two unit system, consisting of four systems with thermal and particulate connectivity between Systems 1 and 2 and also between System 3 and 4. We further suppose that we thermally couple System 2 and 3 so that heat can travel between them. This is illustrated in Figure 3.1.



**Figure 3.1:** A two pair system consisting of four subsystems with subsystems 1 and 2 in thermal and particulate equilibrium, subsystems 3 and 4 in thermal and particulate equilibrium, and subsystems 2 and 3 in thermal equilibrium.

In this case, we have <sup>3</sup>

$$\tau_2 = \tau_1 \left( 1 + \frac{\mu_2 - \mu_1}{\mu_1 - 2 \frac{dU_1}{dN_1}} \right). \quad (1)$$

$$\tau_4 = \tau_3 \left( 1 + \frac{\mu_4 - \mu_3}{\mu_3 - 2 \frac{dU_3}{dN_3}} \right). \quad (2)$$

$$\tau_2 = \tau_3. \quad (3)$$

Then it immediately follows that

$$\tau_4 = \tau_1 \left( 1 + \frac{\mu_2 - \mu_1}{\mu_1 - 2 \frac{dU_1}{dN_1}} \right) \left( 1 + \frac{\mu_4 - \mu_3}{\mu_3 - 2 \frac{dU_3}{dN_3}} \right). \quad (4)$$

<sup>3</sup>This is established in [2].

As  $\mu_1 = \mu_3$ ,  $\mu_2 = \mu_4$ , and  $\frac{dU_1}{dN_1} = \frac{dU_3}{dN_3}$  this relation becomes

$$\tau_4 = \tau_1 \left( 1 + \frac{\mu_2 - \mu_1}{\mu_1 - 2 \frac{dU_1}{dN_1}} \right)^2. \quad (5)$$

Rearranged, this gives us that

$$\Delta\tau_{2n} \approx 2 \frac{\mu_2 - \mu_1}{\mu_1 - 2 \frac{dU_1}{dN_1}}. \quad (6)$$

This result can be generalized to

$$\tau_{2n} = \tau_1 \left( 1 + \frac{\mu_2 - \mu_1}{\mu_1 - 2 \frac{dU_1}{dN_1}} \right)^n \approx \tau_1 \left( 1 + n \frac{\mu_2 - \mu_1}{\mu_1 - 2 \frac{dU_1}{dN_1}} \right) \quad (7)$$

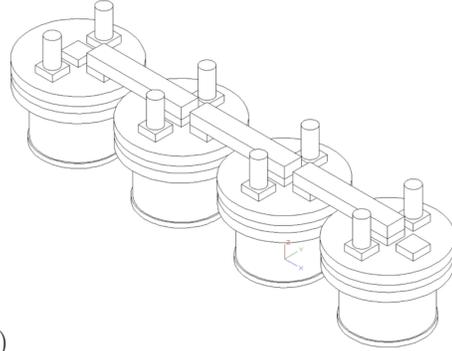
in the case that there are  $n$  connected cells. Rearranged, this gives us that

$$\Delta\tau_{2n} \approx n \frac{\mu_2 - \mu_1}{\mu_1 - 2 \frac{dU_1}{dN_1}}. \quad (8)$$

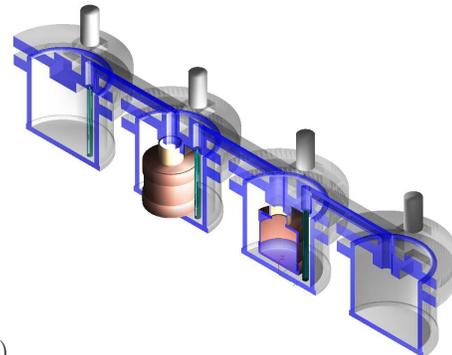
In this way, we can amplify the temperature difference of a single pair of chambers by combining them with additional chambers.

#### 3.2 Enabling the Battery Effect

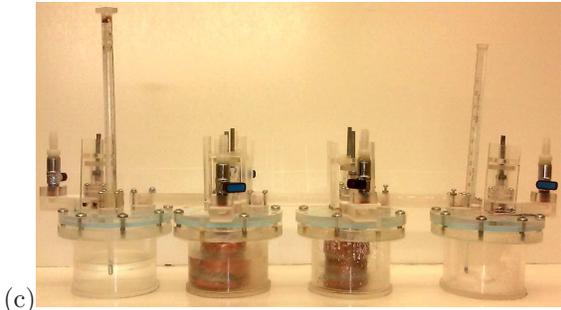
In order to enable the battery effect, we developed a novel architecture for the entrochemical device. The novel architecture, pictured in Figure 3.2, implements two main improvements.



(a)



(b)



**Figure 3.2:** The multi-cell architecture, enabling expanded thermal gradients. (a) the external diagram, (b) the cut-away diagram, and (c) the device.

As indicated in Section 2, a mixing mechanism comprising a tube extending the passageway between the two chambers into the fluid in one chamber is utilized. Additionally, the cold chamber from cell  $n$  is embedded *within* the warm chamber from cell  $n - 1$ . The embedded cold chamber is made from copper and brass components joined together with solder.

As a result of the two changes to the device design, the salt chambers are mixed, preventing formation of the dilute water layer on top of the salt solution. Additionally, the cold chamber from cell  $n$  and the warm chamber from cell  $n - 1$  have virtually the same temperature. As a result, the independent thermal gradients can combine additively to form a larger overall thermal gradient.

## 4 Validation experiments

We conducted validation experiments aimed at confirming the posited performance of the devices. In both sets of experiments, we utilized  $CaCl_2$  salt obtained from food grade calcium chloride. The calcium chloride was either in solution or in the form of degassed crystals. After each experiment, the solution was collected and the crystals recovered by distilling the solution down and reproducing degassed crystals. This additionally confirmed the expected result that the salt could be used over several cycles; our experiments involved more than fifty cycles using the same salt. We utilized unfiltered tap water; no attempt was made to purify the water in any way.

### 4.1 Mixing

In order to conduct mixing studies, 40 grams of a saturated salt solution produced from degassed salt and tap water were placed in the salt chamber. Additionally, 70 grams of degassed  $CaCl_2$  salt were placed in the salt chamber. 120 grams of water were placed in

the water chamber. The apparatus was further enhanced with two completely embedded mercury thermometers that were at least partially submerged in the liquid in each chamber. All experiments were conducted with an ambient temperature in the laboratory of  $22.8^\circ C$ .

In order to initiate the process, a wet vacuum was created in the chambers. We developed a warm vapor wet vacuum process to create the wet vacuum. We generated vapor by applying a vacuum to a container of water at approximately  $43^\circ C$ . The water boils and the low temperature steam is directed through both chambers during vacuum application. Once the wet vacuum is established, the process proceeds and a thermal gradient emerges.

The chamber’s activity is initiated in two different modalities. In one, the vapor is allowed to freely enter the salt chamber and condense. In the second, the vapor enters the salt chamber through a vertical tube whose open end is located below the surface of the salt solution in the salt chamber. As the vapor enters the chamber, it must bubble through the salt solution. The bubbles concurrently mix the salt solution.

We prepared the chamber as described above and ran it in each of the two modes described. The data obtained is given in Table 4.1.

Mixing $\Delta T$ ( $^\circ C$ )	Non-mixing $\Delta T$ ( $^\circ C$ )
$18.3 \pm 0.3$	$10.3 \pm 1.5$

**Table 4.1:** Thermal gradients developed in the electrochemical cell with and without the mixing apparatus installed.

### 4.2 Battery effect

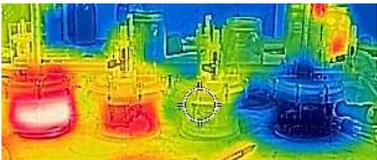
In order to examine how the thermal gradient is enhanced by addition of cells to the device, an electrochemical device was constructed consisting of modular units enabling the connection of up to three electrochemical cells (Figure 3.2). We ran the device in one-, two-, and three-cell configurations in order to document the battery effect in multiunit devices.

Each individual cell is prepared by adding 40 grams of a saturated  $CaCl_2$  solution and 70 grams of degassed  $CaCl_2$  salt to the salt chamber and 120 grams of water to the water chamber. Each cell is enhanced with the mixing tube described above. Each cell is individually brought to a wet vacuum using the warm steam injection process described above. At intervals of thirty minutes, each cell is subjected to an addi-

tional vacuum for thirty seconds at a time<sup>4</sup>. Once all cells have been brought to a wet vacuum, the device is observed until it reaches an equilibrium thermal gradient. An average thermal gradient is reported below in Table 4.2.

$\Delta T$ ( $^{\circ}C$ ) - one cell	$18.3 \pm 0.3$
$\Delta T$ ( $^{\circ}C$ ) - two cells	$30.8 \pm 0.2$
$\Delta T$ ( $^{\circ}C$ ) - three cells	$40.2 \pm 0.3$

**Table 4.2:** Thermal gradients with different configurations of the entrochemical device.



**Figure 4.3:** A thermal image of the three cell entrochemical device.

## 5 Discussion

One of the main difficulties in the development of the entrochemical system as an energy source is the inability to develop thermal gradients large enough to be useful in practice. Systems whose saline solutions could be adequately dried in environmental wind streams tend to generate very small thermal gradients.

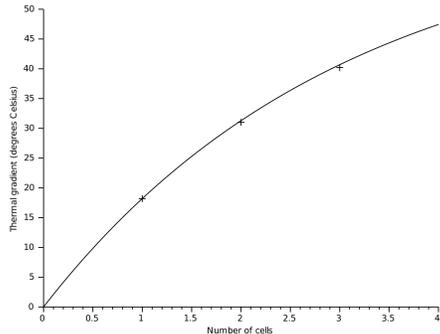
Until this study, we have been unable to adequately build devices that could overcome this limitation. Battery systems seemed to theoretically address all design factors but generated confusing, even contradictory behavior. Thermal gradients in individual entrochemical cells performed as expected, but when linked together, often generated thermal gradients that were negligible or even reversed from expectations. Rather than adding, their effects would often times be in conflict, negating one-another.

In determining the cause of this confusing behavior, we posited that the absorption of water generates a layer of water on the surface of the saline solution. Since saline solutions do not generally mix, this would generate a relatively non-saline layer and could eliminate the effective thermal gradient, leading to the observed confusing behavior. As a result, mixing should eliminate the layer and lead to the expected thermal battery function. The data in Table

<sup>4</sup>It is conjectured that using the vacuum during the run removes non-solvent vapor air that collects on the salt side, having been left in the cell after the initial wet vacuum preparation

4.1 supports this hypothesis as it demonstrates the performance difference with and without the mixing. Not only does the mixed cell equilibrate at a higher overall thermal gradient, but its performance is more reliable; the non-mixed cell seems to be more prone to large performance variations.

Once the mixing mechanism has been added, the performance of the three cell battery is as expected. The battery’s performance more than doubles that of a single cell. As one might expect, the increase in performance is distinctly sub-linear, as can be seen in Figure 5.1.



**Figure 5.1:** The fitted across-device thermal battery gradient data for thermal batteries with varied numbers of cells. The thermal gradients appear to conform well to the fitted curve  $\Delta T = 64.71(1 - e^{-0.33024n})$  where  $n$  is the number of cells.

The data confirm that the battery effect can be used to extend the overall thermal gradient. The sub-linearity is due to thermal leakage along the energy pathway. The device described above in Figure 3.2 is not externally insulated; thermal leakage significantly limits its performance. Our data indicates that the thermal gradient limit of this design is  $64.71^{\circ}C$ , though one can achieve 63.34% of this limit with just three cells.

The achievement of the  $40.2 \pm 0.3^{\circ}C$  represents an important step in the development of atmospheric heat collectors. The salt used in these experiments is  $CaCl_2$ . This salt solution can be dried down to crystals using a solar chimney. This drying effectively reverses the function of the battery, enabling the battery to be re-used.

The fitted curve has a horizontal asymptote at  $64.71^{\circ}C$ . In practice, we would like this asymptote to exceed  $100^{\circ}C$  or even  $200^{\circ}C$ . Our apparatus lacks thermal insulation surrounding the active chambers. In the presence of vacuum insulation, it is expected that this limit can be extended.

It has been shown elsewhere that this process can achieve desalination [1] and that the overall process

can be tied to what has been called a *planetary Stirling engine* [2]. It is worth noting that such a process of desalination is achieved entirely without the use of fossil fuels. As we can now generate thermal gradients of sufficient magnitude to enable distillation, the utilization of an atmospheric heat collector to achieve distillation is a realistic possibility and may enable the growing and present need for desalination worldwide. That it can be achieved without expensive or sophisticated materials or fuels makes it the only realistic option. It will be interesting to develop advanced versions of this technology and to see where this fits in the broader field of seawater desalination[10].

## 6 Conclusion

This paper has demonstrated a mechanism for extending the thermal gradient in a simple entrochemical system. The mechanism includes a mixing mechanism for breaking the water layer that forms on the top of the salt solution. Using a saturated  $CaCl_2$  solution, it was demonstrated that this mechanism successfully enhances the performance of a single entrochemical cell, yielding performance that is more consistent and produces larger thermal gradients than an equivalent device of the same design. We constructed a thermal battery system comprising up to three nested cells. Again using a saturated  $CaCl_2$  solution, we demonstrated that the battery system is capable of expanding the thermal gradient by a factor of 2.19 with only three complete cells. The thermal gradient achieved with three cells is  $40.2 \pm 0.3^\circ C$ .

It is expected that better thermal insulation would significantly improve the limit enabling the three-cell unit to achieve gradients greater than  $50^\circ C$ .

## References

- [1] S. Kazadi, Y. Hong, C. Chau, A. Chaudhary, A. Chaudhary, J. Park, J. Liu, M. Kim, D. Kim, S. Kim. *Desalination powered by entropy*. **Proceedings of the Asian Conference on Sustainability, Energy, and the Environment 2011**, Osaka, Japan, June 2-5, 2011.
- [2] S.Kazadi, A. Schwartz, J. Huang, R. Goy, C. Koo, S. Choi, J. Lim, A. Koh, J. Choi, C. Koh, J. Wang. *Collecting energy from a planetary entropic Stirling engine*. **Proceedings of the Asian Conference on Sustainability, Energy, and the Environment 2013**, Osaka, Japan, June 6-9, 2013.
- [3] S. Kazadi, R. You, M. Kim, M. Kim, M. Kim. *A passive regulated thermal gradient device and application to unpowered refrigeration and heating*, **Proceedings of the Renewable Energy Conference 2010**, Yokohama, Japan, June 27-July 2, 2010.
- [4] C. Kittel and H. Kroemer. **Thermal Physics**. W.H. Freeman and Company, New York, 1980.
- [5] M. Olsson, G. Wiek, and J. Isaacs. *Salinity gradient power: utilizing vapor pressure differences*. **Science**, 206 (4417), pp.452-454, 1979.
- [6] Y. Emami, S. Mehrangiz, A. Etemadi, A. Mostafazadeh, S. Darvishi, *A brief review about salinity gradient energy*, **Int. J. Smart Grid Clean Energy**, 2, pp. 295–300, 2013.
- [7] S. Kazadi, K. Park, J. Jeon, A. Lew, S. Song, J. Jung, B. Kim, B. Luo. *Improving energy scavenging capacity via a vertically configured closed-circuit PRO system*. **Proceedings of the IAFOR North American Conference on Sustainability, Energy & the Environment Conference 2014**, Providence, Rhode Island, September 11-September 14, 2014.
- [8] S. Skillhagen, J. Dugstad, R. Aaberg. *Osmotic power — power production based on the osmotic pressure difference between waters with varying salt gradients*. **Desalination**, 220, pp. 476–482, 2008.
- [9] S. Skillhagen. *Osmotic power — a new, renewable energy source*. **Desalination and Water Treatment**, 15: 271-278, 2010.
- [10] M. Elimelech and W. Phillip. *The future of seawater desalination: Energy, technology, and the environment*. **Science** 2011, 333, 712–717.