MATHEMATICAL MODELING AND SIMULATION OF HEAT TRANSFER IN A THERMAL BATTERY

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Abstract. Thermal batteries are primary disposable systems specially designed to develop a high energy density in during a short period. Differently from the classical electrochemical systems, the electrolyte of such batteries is solid at room temperature, which make them inert until they are heated to high temperatures (around 500°C), when the electrolyte melts and begins to exhibit enough ionic mobility to establish electric current. The present work was devoted to developing a transient model of the heat generation and propagation within a second generation thermal battery, aiming the creation of a tool suitable for the research and development of such systems. The commercial CFD software Phoenics® was used and, through a typical finite volume approach, the related 2-D transport equations were solved, giving the time-dependent temperature profiles. The results show that the temperature of pseudo equilibrium state of these studied batteries are in accordance with the temperature related in the literature, and the fusion of electrolytes is a process virtually instantaneous when compared with the time to reach that state, allowing in this way to advance that the generation of electrical current occurs immediately after the termites actuation.

1 INTRODUCTION

Thermal batteries are special electrochemical systems that a great amount of energy is carried out during a determined period of time, having as a main characteristic it’s functioning at high temperatures. The electrochemical couple, the cathode and the anode, is juxtaposed to an electrolyte that, at room temperature, is solid and inert. The start up is made by an electrical squibb that initiates a pyrotechnical material (thermite) placed between the cells. The internal temperature rises quickly, melting the electrolyte and the starting of electrochemical reactions, generating values of current density greater than the ones of typical electrochemical systems, as illustrated in figure 1.
The advances in the related technology increased the usage of such devices, mainly because different uses of cathodic and anodic materials. Such improvement allowed the construction of greater and more complex cells, which needed laboratory tests to optimize their performance. The costs and time demands for the construction of these bigger batteries (up to hundreds of cubic inches), as for the related tests, are considerable and since the system performance depends on a reliable thermal project, a computational model able to simulate this project is of a great interest.

Thermal batteries main advantages are: long shelf life time (up to 25 years), high reliability and great resistance to exposition to dynamic charges, such as shock, vibration, acceleration and spin. These characteristics allow applications in devices for defense and airspace apparatus such as emergency fixtures, on-board energy for start up, guide and control of missiles and additional energy of airspace missions and satellites.

Because it is a sensible and strategic technology, there is not enough scientific works available in the open literature about thermal batteries, being the greater number of these information obtained from technical report, which access is limited, as those existent in Sandia laboratory and in Brazilian Army Technological Center. WU studied the heat dissipation on lithium batteries Schoeffert modeled the heat transfer into a third generation thermal battery and compared the results obtained by simulations with experimental measurements.

In the present work, the heat transfer of a second generation thermal battery is studied. A transient model of the heat generation and its propagation within thermal battery is carried out, using a CFD code. The simulations indicate that maximum electrolytes temperatures are similar to temperatures related in the literature as the produced by directly burning of them. The temperatures simulation in function of time for thermal batteries of second generation are similar to the results published by Schoeffert.
1.1 The main elements of a second generation thermal battery

The electrochemical systems used here is the second generation thermal battery that is Li/FeS₂ and Ca/CaCrO₄ systems. It works at average temperature of 600°C and the thermitic mixture used is composed of an oxidant, barium chromate, and a fuel, metallic zirconium. Their main constituent elements are summary described as follows:

**Thermite**: Thermite is compound of zirconium and barium chromate sustained by asbestos fiber in a disc shape. The thermite photograph can be seen in figure 2.

![Figure 2: A photograph of thermite](image.png)

According to literature², the analyses of ashes resulting from combination of thermite Zr/BaCrO₄ in inert atmosphere of argon by X-ray diffraction technique suggests a hypothetic decomposition reaction as bellow:

\[
3\text{Zr} + 4\text{BaCrO}_4 \rightarrow 3\text{ZrO}_2 + 4\text{BaO} + 2\text{Cr}_2\text{O}_3
\]  

(1)

In addition, according to the same researcher, the standard heat of reaction of the above reaction at 298K (\(\Delta H^{0}_{298}\)) is:

\[
\Delta H^{0}_{298} = -476.3\text{Kcal/mol de BaCrO}_4
\]  

(2)

**Cathode**¹: The cathode is made with applying the electrochemically active material (as an ink) - also known as cathodic mixture - that is dispersed over a disc of pure nickel. The ink, by its turn, is done adding the cathode mixture (a powder) to a certain amount of a liquid matrix. The electrochemically active material is a mixture of CaCrO₄ and SiO₂ and the liquid matrix is made of trichloroethylene and dimethylphthalate.

**Anode**¹: It is made by pure metallic calcium.
Electrolyte**: The electrolyte of the thermal battery is a mixture of inorganic salts that form an eutectic mixture applied on a glass fiber cloth for its retention.

2 TRANSIENT MODEL CONSTRUCTION

Due to the cylindrical symmetry of thermal battery, the coordinate system used in this study was the cylindrical coordinate (R, θ and Z). The virtual domain has the dimension of the steel covering of batteries, differing only in height, according to type of batteries in question (3, 6 or 12 unitary cells). In all studied cases the dominium was considered adiabatic.

All models developed here employed, as an initial condition, the instant in which the thermite was ignited by the squibbs linked to the wall propagators; therefore the ignition of these propagators and the propagation of the burning front up to the squibbs are out of the objectives of this work and weren’t computed in this model (besides, all these events happen in a very small period of time and can be neglected).

It is known from the literature that high temperature variations are expected into the thermal battery**, so the hypothesis of constant thermal conductivities and heat capacitances does not apply to the model developed here. Because of that, mean values for those entities (for each substance) were calculated for an arbitrarily chosen temperature interval from 298 K to 902 K, assuming that this is the temperature range in the adiabatic system.

2.1 Thermite modeling

The thermite is a heat source responsible for melting the thermal battery electrolyte, leading to the device activation. Due to its vital importance and because its ignition was considered the initial simulation time for this study, this part of the system was modeled separately.

As a first hypothesis, the burning velocity of Zr/BaCrO$_4$ mixture was assumed about 100 m/s. Attempts of accurate measurements of this parameter were tried, but up to the end of this work, no conclusive results could be found. As there are two propagators in the battery and assuming, by hypothesis, that they act on two diametrically opposite borders simultaneously, one can calculate:

$$t = \frac{R}{V} = \frac{28.25\text{mm}}{100,000.00\text{mm/s}} = 2.82 \times 10^{-4} \text{s}$$

Simulations carried out using the above values showed that the temperatures reached in the neighborhood of thermite would be greater those related by literature. As the parameter of major uncertainty is the burning time, many simulations were made varying this parameter in the interval 1x$10^{-1}$s to 9x$10^{-1}$s; the value 5x$10^{-2}$s seemed to produce results that are the most concordant to the ones in literature. One knows also from literature that the amount of heat produced in the burning of a thermite is around 12140 J.

So, the heat source of thermal battery was modeled as a pulse function. On Phoenics®, heat pellets were defined to be energy sources following the function shown in the figure 3.
2.2 Modeling of cathode and anode

The final composition of each substance in these elements was calculated and the average thermal conductivity and heater capacitance were obtained for each of them. On Phoenics® library, two new materials were created and labeled “cathode” and “anode” with their respective properties calculated as described.

2.3 Electrolyte modeling

The KCl-LiCl eutectic latent heat of fusion was calculated as a mean of the latent heat of fusion of each salt, weighted by its mass. Phase transition was modeled considering that the fusion occurs almost instantaneously (less than 0.5 s) and at constant temperature. This assumption was made, because:

1. Very little thickness of electrolyte (0.10mm) allows one to adopt the hypothesis that this element fuses completely – there is no need to establish a fusion mushy region in such a thin material.

2. The fusion occurs necessarily at constant temperature, once the electrolyte is an eutectic.

3. The heat propagation into the thermal battery occurs mainly by diffusion, and convection can be neglected.
2.4 Thermal battery remaining elements modeling

The remaining elements of the thermal battery were treated as composed of single substances, it means, they had their properties estimated according to their constituent material. This is the case of the activation base (made of bakelite), of the mica insulation sheets, of the separators (made of steel), of the negative pole (a nickel disk) and also of the fiberfrax that fills the empty space that appears after the device mounting. All these elements could be found in the original library of Phoenics®, besides is the fiberfrax, which was then putted in it taking as base the data obtained from furnisher page for casting fiber.

2.5 Thermal battery model “construction” in Phoenics

Since that the materials constituents of thermal batteries elements were added to Phoenics library, the transient model of a three elements battery could be conducted in the graphic interface named “VR-EDITOR”, as shown in Figure 4.

![Figure 4 - Thermal battery with three elements implemented in VR-EDITOR](image)

Initially, a cylindrical coordinates system was chosen with zero internal radio. Then, the dominium was defined as a steel cylinder with the same dimensions of the outer steel case. Additionally, it was considered adiabatic and invisible to allow the visualization of the internal batteries elements.

Finally, each battery element was created in its real dimension, respecting their true colors and using the materials in the software library. All heat pellets were defined as transients sources of energy that have the behavior of pulse function previously discussed. With that, all thermites are ignited in the initial simulation time and have the same burning time. The fact that all elements are pressed together was respected, leaving no void space among them. The space between the active elements and the outer case was “filled” with fiberfrax, defined as the domain material.

3 SIMULATION OF THREE ELEMENT THERMAL BATTERY

The three element battery has a total of seven thermitic elements and nine electrolytes. The total computational processing time was around six hours in an Athlon XP 1000 MHz with
256Mb of RAM. The simulation showed that the pseudo equilibrium temperature of system (PET) is around 442 °C, as shown the figure below.

![Figure 5 PET of calculated system: 442° C](image)

According to literature, the optimum operation temperature (OOT) of this battery is between 550 °C and 650 °C, which can indicate that, in the three elements thermal battery the increase of a thermite could increase its efficiency. We should emphasize that the OOT related in the literature must not be understood as the temperature of better functioning. In fact, as one can see in these simulations - and could even be anticipated by the device anisotropy and by the existence of refractory materials in it - a situation of thermal equilibrium only can be reached in a time much greater then the one for the total consumption of materials with electrochemical activity. The OOT, however, seems to be calculated in literature with thermodynamics considerations, so as to establish a parameter for calculation of the best amount of thermites. In this way, its comparison with the values of PET (Pseudo Equilibrium Temperature) obtained in this work will have a qualitative purpose and not a conclusive one, for the acceptation of the experimental arrangement in question.

In figure six to ten one can observe the evolution of temperature profile versus the time, respectively at instants 4.44s, 259.40s, 745.50s, 1121.00s and 5505.00s, randomly chosen as simulation times.

![Figure 6 - Temperature profile in t = 4.44 s](image)
Figure 7 - Temperature profile in $t = 259.40$ s

Figure 8 - Temperature profile in $t = 745.50$ s

Figure 9 - Temperature profile in $t = 1121.00$ s
The simulation revealed that temperatures developed in thermites neighborhoods, after its burning is completed, is much greater than the equilibrium temperature, indicating that the elements next to thermit (for instance, electrolytes) are subject to temperatures picks that can reach high values. This fact is due to the great heat combustion of thermites associated to its burning speed, increased by the final pressing operation of the device. Another interesting way of visualizing transient temperature profiles is to turn visible only the objects of interest. The figures eleven to fourteen illustrate that electrolytes heat quickly after thermites ignition, allowing estimating the time required for melting the eutectic KCl-LiCl.
Figure 12 - Electrolyte temperature profile in t=0.80s

Figure 13 - Electrolyte temperature profile in t=1.20s

Figure 14 - Electrolyte temperature profile in t=2.00s
One could notice that in $t = 1.2s$, the electrolyte temperature exceeds the fusion temperature of eutectic (350 °C). This shows that that the activation of the battery is almost instantaneous, which is also observed in laboratory tests.

4 SIMULATIONS OF THERMAL BATTERIES OF SIX AND TWELVE ELEMENTS

Simulations similar to those presented above were also carried out for thermal batteries of six and of twelve elements, which confirmed that the electrolyte fusion is faster in relation to necessary time for system to reach the PET and that these values are in accordance with the OOT found in the literature for these kind of batteries. Table one resume these values:

<table>
<thead>
<tr>
<th>Number of Elements</th>
<th>Calculated PET</th>
<th>OCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>550°C - 555°C</td>
<td>550°C - 650°C</td>
</tr>
<tr>
<td>12</td>
<td>643°C – 684°C</td>
<td>550°C - 650°C</td>
</tr>
</tbody>
</table>

Table 1: OCT x PET

5 CONCLUSIONS

Despite thermal batteries have been invented in the 40’s, its improvement and optimization are still object of study and research. As material specially designed for defense applications, scientific articles are scarce, incomplete and do not reveal fundamental technical details for complete technology comprehension.

As the construction of models, the results in this work indicate that the simplifications employed and the methodology adopted were adequate, because simulation results quite fitted the ones available in literature, as small battery auctioning time - around 1.0 s or less, and maximum electrolytes temperatures (elements near to thermites) that are similar to temperatures related in the literature as the produced by directly burning of them.

The PET of second generation batteries produced by Brazilian Army Technological Center (CTEx) modeled in this work are into or quite close to OOT related in literature. One could conclude yet that simulation in function of time for thermal batteries of second generation are similar to the results published by Schoeffert\(^9\) taking into consideration the particular characteristic of each system.

6 REFERENCES


